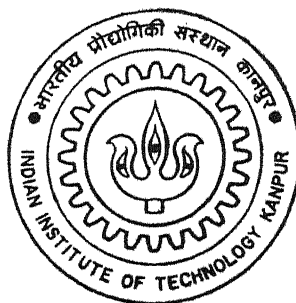# MODIFICATIONS IN UNIDIRECTIONAL PREPREG MAKING MACHINE AND CHARACTERIZATION OF PRODUCTS

by

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Nuclear Engineering & Technology Programme

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

JANUARY, 1995

MODIFICATIONS IN UNIDIRECTIONAL PREPREG MAKING MACHINE AND CHARACTERIZATION OF PRODUCTS

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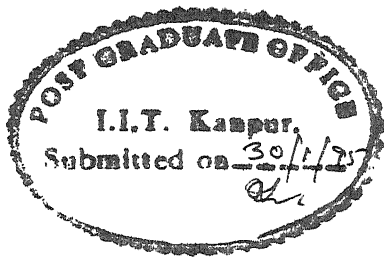
CERTIFICATE

This is to certfy that the thesis entitled "*MODIFIACATIONS UNIDIRECTIONAL PREPREG MAKING MACHINE AND CHARACTERIZATION PRODUCTS*" by Lt. A.P.Kulkarni is a record of work carried under my supervision and has not been submitted elsewhere fo degree.

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DEDICATED TO MY MOTHER

ACKNOWLEDGEMENT

ABSTRACT

This work has been undertaken on indigenous development of unidirectional prepreg making machine at E.S.A.laborator Mechanical engineering department, I.I.T. Kanpur. The modifications have been carried out in the existing machine so as to improve the product quality. These include modified design of resin bath, heating of rotating release film rollers, fitment of release film guides and of roving stand eye-lids.

Formulation of epoxy resin mixture alongwith the basic chemistry involved in the process, has been studied. A suitable epoxy resin mixture has been adopted in line with the same being followed internationally. Preparation of prepregs using glass-fibers and epoxy resin mixture has been undertaken. The characterization of prepregs has been conducted to evaluate performance of the machine.

Interlaminar fracture toughness enhancement, using elastomer (CTBN) modified epoxy resin mixture is attempted. Contrary to the expectation, there has not been any significant improvement in the impact induced damage and interlaminar fracture toughness.

The laminates prepared through prepregs have been characterized to determine fiber volume fraction, tensile strength, compressive strength, interlaminar G_{Ic} and through the thickness J_{Ic}. The results obtained during characterization have been compared with corresponding values available in literature. The value of the tensile strength for cross-ply laminates is about 30 percent less than the corresponding value available in literature, while for unidirectional laminates the difference is 24 percent. The value of the compressive strength for cross-ply laminates is about 10 percent less than the corresponding value available in literature.

CONTENTS

CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

Composite is a combination of two or more distinct constituent materials - a reinforcing agent and a matrix with an aim to achieve specific properties. The properties of the composite can not be obtained with any of the constituent materials present alone.

In general, the reinforcing agent can be either fibrous, powdered, spherical, crystalline and either an organic, inorganic, metallic or ceramic material. In this work polymer matrix fibrous composites have been considered

According to their structure and behavior, polymers can be classified as thermoplastics or thermosets. Thermoplastic polymers are those which can be hardened and softened by increasing and decreasing the temperature respectively. Examples include polyethylene, polystyrene, nylons. Thermosetting polymers do not soften but decompose on heating. They can not be reshaped once solidified by a crosslinking process. The various types of thermosetting polymers are epoxy, polyesters, polyimides [1].

Polymer composites, because of their attractive properties such as light weight, high strength, high modulus, design flexibility; find their applications in various fields like aerospace industry, automobile industry, marine construction and sports goods.

1.2 FABRICATION OF FIBROUS COMPOSITES

The fabrication of composites consists of impregnation of fibers

with matrix so as to wet the fibers completely. In case of thermosetting matrix composites material formation accomplishes during moulding due to their curing characteristics. However, in case of thermoplastic matrix composites, the first step is to form the composite and in the second step it is moulded to the required shape.

Fabrication processes for composites can be broadly classified as wet forming processes and processes using premixes or prepregs The wet forming process consists of combining fibers and matrix together and curing is completed in one step. These include hand lay-up, filament winding, pultrusion and injection moulding [2].

In the dry forming process, forming and moulding operations are uncoupled. The first step involves impregnation of fibers with matrix so as to form semi-cured raw material - prepreg tapes, which are subsequently used for product lay-up and final curing is accomplished by applying designated temperature and pressure. The various techniques of wet forming process as well as laminate making using prepregs are briefly covered in the following sections.

1.2.1 Hand lay-up technique

In this technique the raw materials used are fibers (e.g. glass-fiber mat, fabric) along with thermosetting resins (e.g. epoxies, phenolic, polyesters). The first step of the process is mould preparation with desired surface finish. This is followed by application of a gel coating which forms the outer surface of the completed laminate. Finally, fiber glass in the form of chopped strand mat and appropriate resin mixture are applied onto the mould. Entrapped air is removed by using serrated rollers by compacting material against the mould surface.

1.2.2 Filament winding

This technique is best suited to manufacture surfaces of revolution such as pipes, tubes, cylinders and spheroids. In this method, rovings from creels are passed through resin bath to impregnate the fibers and are then wound over a rotating male mandrel. The winding angles and location of fibers are controlled with the aid of special machine to match the traversing speeds with mandrel rotation. The various types of mandrel angles are longitudinal, helical and circumferencial. The main advantage of this method is high production rates due to process automation [1,3].

1.2.3 Pultrusion

This technique is used to produce constant cross-section profiles like rods, tubes. Rovings from creel are pulled by a driving mechanism through resin bath. On the line, the shape preformer removes excess resin and entrapped air. The product is then cured continuously in heated die and finally cut with a cut-off saw [2].

1.2.4 Injection moulding

This process is employed for the production of parts with short-fiber reinforced thermoplastics [2]. The raw material used for injection moulding is a compound of the resin and fibers in a pelletized form and is prepared in a separate process. There are two methods of forming moulding compound -extruder compounding and strand coating. In the former process, the chopped fibers and resin are fed directly into an extruder for mixing. The later consists of passing the rovings of fibers through an extruder die head so as to coat and impregnate fibers with resin which are subsequently cooled in a water bath and cut into required lengths

1.2.5 Laminate through prepregs

This process is divided into two steps, (i) making prepregs and (ii) producing components from prepregs. These processes are usually carried out by two separate agencies. Prepregs, which is semi-cured product in thin sheet form, are used to prepare laminate. For making a required component the prepregs can be hot-pressed between two halves of matching dies by an user. The process is suitable for high production rates but initial capital cost for making a die is high. The pressure bag technique using a single die avoids high cost of matching dies. In this procedure, the stack of prepregs is enclosed within a pressure bag and is placed over the die. The entire set-up is inserted into an autoclave where prepregs are pressed by nitrogen gas at high temperature and pressure. Thus, for pressure bag moulding to be effective and advantageous, it is necessary to make prepregs. Secondly, storing and transportation of prepregs for import is tedious, risky and costly, because they are required to be maintained at temperature below zero degree celsius. Therefore, it is mandatory that prepregs are produced in the region where FRP components are manufactured.

1.3 TECHNIQUES OF MAKING PREPREGS

Prepreg is either ready-to-mould material in sheet form or ready-to-wind material in roving form, which may be cloth, mat, unidirectional fiber or paper impregnated with resin and stored for use. The resin is partially cured to a B-stage and supplied to the fabricator who lays up the finished shape and completes the cure with heat and pressure.[3]

As far as impregnation of fibers is concerned, the process can be divided into two methods - impregnation via solution and hot-melt technique. Though the impregnation of fibers is better in case of solutions method, it poses the problem of solvent removal. Residual solvent produces prepreg which is too tacky and difficult

to handle. Also, it causes voids in the resultant composite deteriorating its mechanical properties. The use of hot-melt technique allows the resin/fiber ratios to be accurately set. Also, constant tackiness suitable for automated production is determined by resin system alone. The present trend favors use of hot-melt technique for unidirectional prepregs and resin solutions for fabric prepregs. Prepregs from woven fabric are easier to manufacture, because fibers are locked into their positions. However, unidirectional prepregs are more difficult to make.

Prepreg machines with woven fabric are produced in India (Genset, Ahmedabad). Also, at several places these machines are being used (Tech Invest Pvt. Ltd, Hardawar. DRDO, Hyderabad), however, their exploitation is restricted to in-house use only.

Prepreg machines with non-woven unidirectional fibers are still not made in our country. The various imported machines are expensive and require continuous import of special raw material such as special grade release paper between which prepregs are sandwiched. Thus, it is the need of the hour to develop indigenous prepreg making machines so as to form the product to meet the requirements, conditions and constraints of our country. It is also necessary to develop proper epoxy blends that would provide right degree of partial curing and tackiness to the prepregs, because the technology is not readily available or open to obtain them directly.

Study of the imported prepreg machine at IPCL

The imported prepreg machine at IPCL is based on hot-melt technique technique and makes prepregs in different steps. In the first step, appropriate epoxy resin formulation is carried out in the resin kitchen. In the second step, a thin layer of hot-melt epoxy resin mixture is applied on special grade release paper. As shown in Fig.1.1, this process consists of applying hot-melt resin to release paper through doctoring device and covering the resin layer with protective film from top. The resultant product is

STAGE 1. FORMING RESIN FILM:

HOT-MELT RESIN

PROTECTIVE FILM

DOCTORING
DEVICE

COOLING ROLLER

BACKING
PAPER

ROLL WITH RES.
FILM & BACKIN(
PAPER
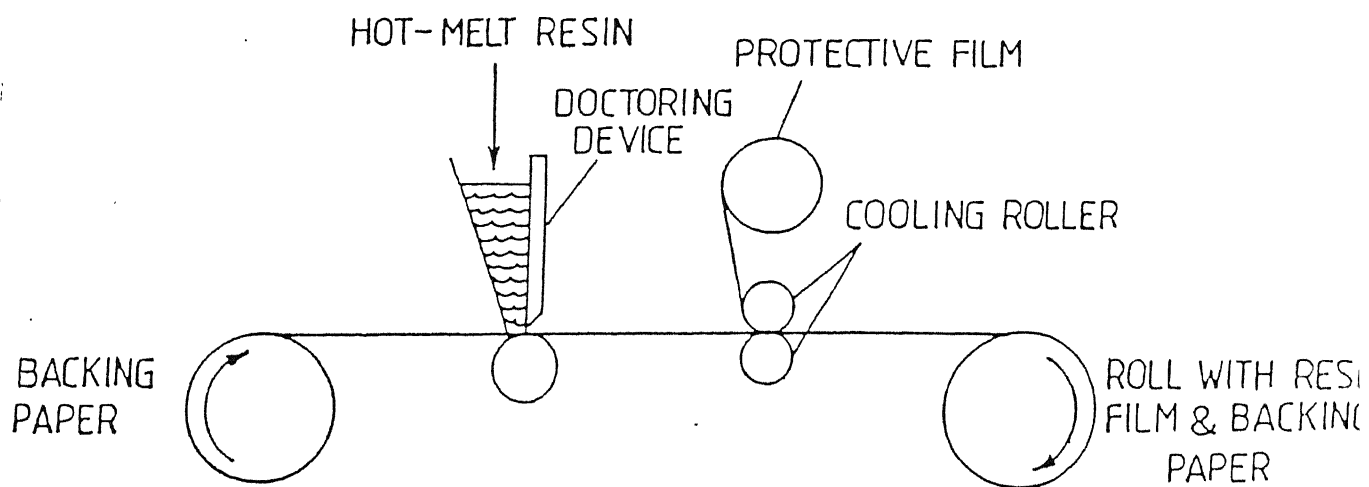
FIG. 1.1   COATING OF SPECIAL GRADE RELEASE PAPER WITH
EPOXY RESIN MIXTURE IN IPCL PREPREG MACHINE.
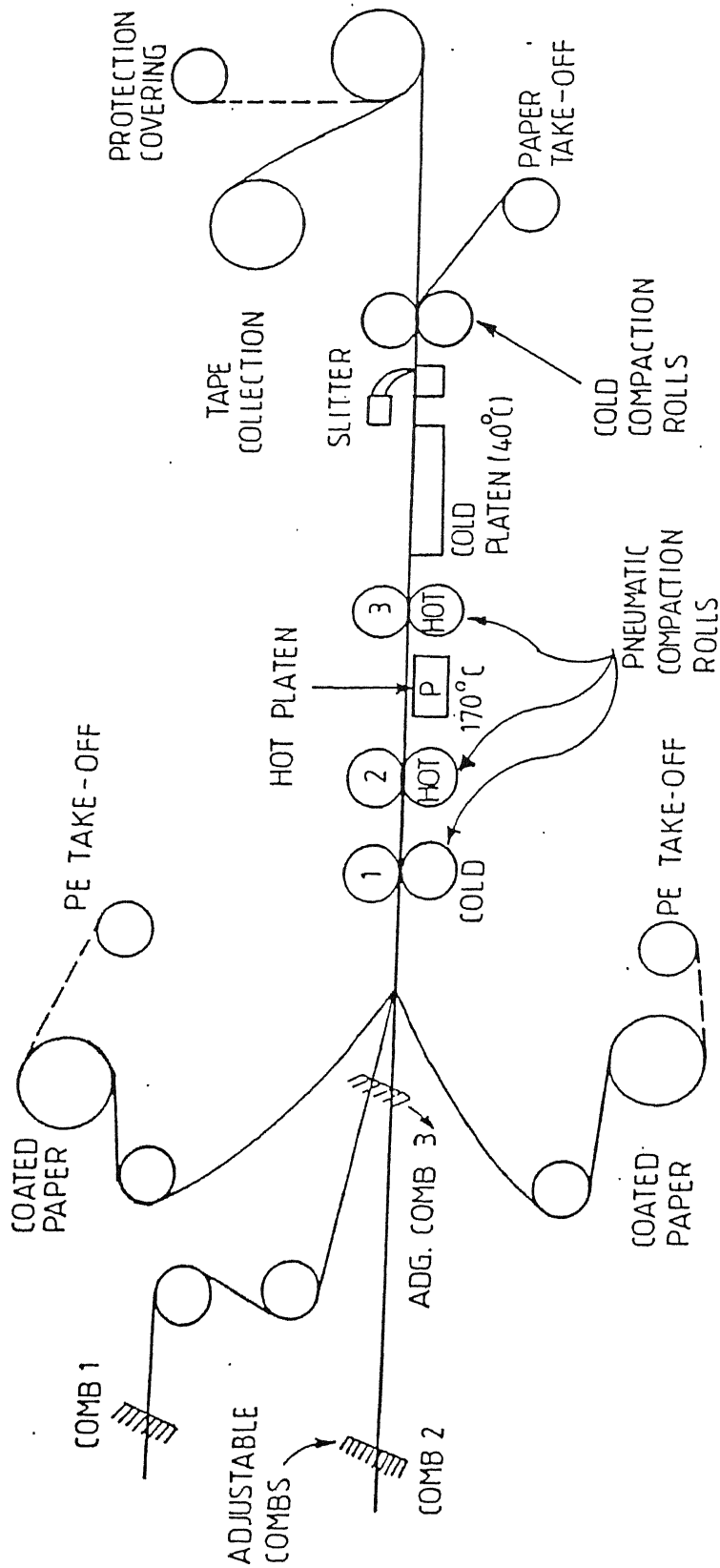
FIG. 1.2   SCHEMATIC LAYOUT OF IPCL PREPREG MACHINE.

7

spool.The third and final step, as shown in Fig.1.2, produces th
prepreg. Rovings from cheese are collated initially through comb
1 and 2 to form two fiber tapes, which are merged near adjustabl
comb 3. This is followed by application of coated paper:
(obtained through a separate machine shown in Fig.1.1) on eithe:
sides of the fiber tape. It is then passed through three sets of
pneumatic compaction rollers. The first set of rollers is not
heated while the other two sets of rollers are heated to 170°C.
Transfer of resin from paper to fibers takes place through heated
compaction rollers and hot platen located in between the hot
rollers 2 and 3 and maintained at the same temperature of 170°C.
Prepreg tape thus formed is passed through cold platen to arrest
further curing. A slitter is provided to remove sides of prepreg
tape on the line. Then the prepreg tape is covered with
protective layer and is wrapped on a collection roll.

1.4 PREPREG MACHINE AT E.S.A.LAB, I.I.T.KANPUR

1.4.1 Objective of the project

The main objective of the project is to design and develop
machines for making prepregs and to transfer the technology to
industries. It is also necessary to characterize the product so
as to evaluate the performance of the machine.

1.4.2 Description

The machine has been designed in such a way that all the processes
involved in preparing the prepreg tape occur on-line. Referring
to Fig.1.3, the rovings are pulled out of the cheese that are
mounted on a stand. The fibers are then passed through an
adjustable collator with individual slot to each roving to collate
them as per the required width of the prepreg tape. The collated
fibers are then wetted with epoxy resin mixture in a resin bath
consisting of three squeeze rollers parallel to each other and
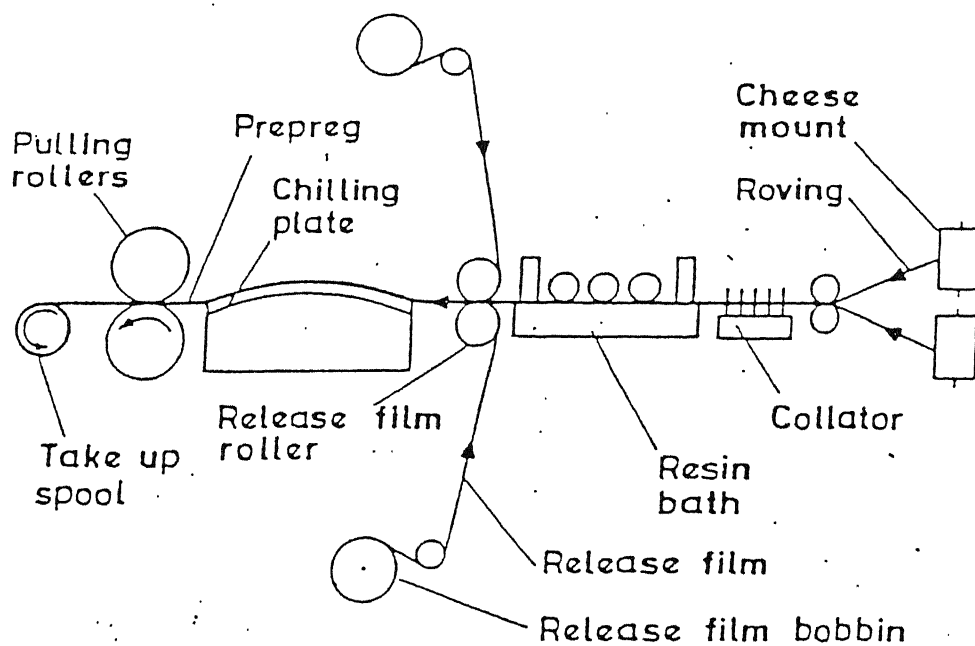
FIG. 1.3   ORIGINAL LAYOUT OF PREPREG MACHINE AT E S A
LABORATORY MECHANICAL ENGG. DEPARTMENT I I T
KANPUR.

placed normal to the direction of fiber motion. The tape of fiber passes between the rollers and flat base plate. The gap between the bottom of the rollers and the top of the base plate is controlled to be small, of the order of the thickness of the prepreg tape, so as to squeeze the epoxy resin mixture. The temperature of the resin bath is controlled to have desired curing of the epoxy resin mixture. Immediately after the prepreg tape comes out of the resin bath, there is a release rollers assembly that applies release films to both the surfaces of the tape. Then the tape passes over a chilled aluminium plate so that the further curing of the resin is arrested. The rubber clad pulling rollers apply the pulling force on the tape. Coupled with the motion of the pulling rollers is a spool that rolls up the prepreg tape.

1.4.3 Need for modifications

The performance of the prepreg machine has been satisfactory except for following problems :
. Curing of epoxy resin mixture in resin bath.
. Coagulation of fibers within the resin bath.
. Incomplete wetting of fibers.
. Splitting of fibers in lateral direction.
. Rubbing of fibers on the edges of roving stand.
. Lateral shifting of the release films during a run.

To overcome these difficulties, the prepreg machine has been modified as described in chapter II.

1.5 INTERLAMINAR FRACTURE TOUGHNESS OF COMPOSITES

Delamination or interlaminar failure is a common failure mode observed in composite material. In order to enhance their fracture toughness, toughened matrices using elastomeric modifiers, have been explored for last two decades[4]. Bucknall C.B. [5] reported the techniques of toughness enhancement by

modifying thermosetting resins with rubber or thermoplastics or a ductile material. Although significant improvement in fracture toughness of epoxy was observed by addition of elastomer, this effect was not proportionately transferred to carbon fiber composites, where only modest improvements in fracture toughness were achieved 0.28 kJ/m^2 for unmodified epoxy composites against 0.49 kJ/m^2 for an elastomer toughened composites . Fracture toughness of woven fiber composite was reported to be 100% higher than the value for unidirectional composites made from CTBN toughened liquid DGEBA epoxy resin, while the fracture energy of woven carbon fiber impregnated with modified liquid DGEBA epoxy is several times higher than the value measured for a unidirectional composite made from carbon fiber and unmodified liquid DGEBA resin [4].

1.6 OUTLINE OF THE PRESENT WORK

In the present work, existing prepreg machine has been modified as described in chapter II. Development of proper epoxy blends, prepreg preparation and characterization have been dealt with in chapter III. Preliminary work to enhance interlaminar fracture toughness of the resultant laminate by using modified epoxy resin mixture, has been covered in chapter IV. Chapter V is devoted to laminate preparation and their characterization. The work has been concluded in chapter VI with suggestions for future work.

CHAPTER II

MODIFICATIONS IN PREPREG MAKING MACHINE

2.1 INTRODUCTION

In the original layout of the machine, as described in chapter 1 certain difficulties were experienced as follows:

. During the continuous run of the machine, the epoxy resin mixture cures at temperature of 85-90°C of the resin bath.

. Fibers coagulate between squeeze rollers and base plate of resin bath.

. Fiber tape, after it comes out of the resin bath, often splits.

. Epoxy in the resin bath is not uniformly heated by the electric heating coil at its base plate.

. Wetting of fibers is not always 100%.

. Release films, between which the prepreg tape is sandwiched tend to shift sideways so much so that its edge may slip over the end of the release roller.

. Fibers tend to rub along the edges of roving stand as well as to each other.

. The condensed water accumulates on the surface and sides of chilling plate.

To overcome these problems, the prepreg making machine is modified as described in the following sections. The specific advantages after carrying out each modification have been stated.

2.2 MODIFIED RESIN BATH:

To avoid curing of epoxy resin mixture in the resin bath, the wetting and partial curing operations need to be uncoupled. This can be achieved by separating resin bath into two different sub-assembles viz. resin bath for fiber wetting at considerably lower temperature of 55-60°C and heating chamber for partial

curing at higher temperature of 120-150°C.

In the original deign of resin bath, as shown in Fig.2.1(a), three squeeze rollers parallel to each other and placed normal to the direction of fiber motion were used. Rovings were passed in a straight line between squeeze rollers and flat base plate. The heating of the resin bath was carried out with electrical heater located inside the flat base plate. As mentioned in the previous section, coagulation of fibers between squeeze rollers and base plate resulted in damage to fibers and subsequent breakage of fibers. In such situations, the prepreg machine was required to be stopped. Due to localized heating of the resin bath, the viscosity of epoxy resin mixture inside the resin bath could not be maintained same through out.

The modified design of resin bath, as shown in Fig.2.2 (a) and (b), ensures its uniform heating with water jacket heating arrangement. This consists of water bath, pump and hose connections. The temperature of the water bath can be controlled with a temperature controller.

The modified resin bath, incorporates four different rollers, namely - guide roller, wetting rollers and a set of doctoring rollers. All the four rollers are made of brass and polished to have very smooth surfaces. The guide roller and doctoring rollers are of 24mm diameter. They are fastened to the top plate of resin bath with cap screws. The gap between doctoring rollers is controlled to be small (e.g.0.2 mm) of the order of the thickness of prepreg. The wetting roller is of 9 mm diameter with its lower surface mounted at about 2-3 mm from the bottom plate of resin bath. It is fixed onto the top plate of the resin bath with the help of bridge assembly consisting of two mild steel roller holder angles.

An adjustable base plate with slotted holes has been fitted, so that distance between the resin bath and release film rollers can be varied. This arrangement allows to set an optimum distance
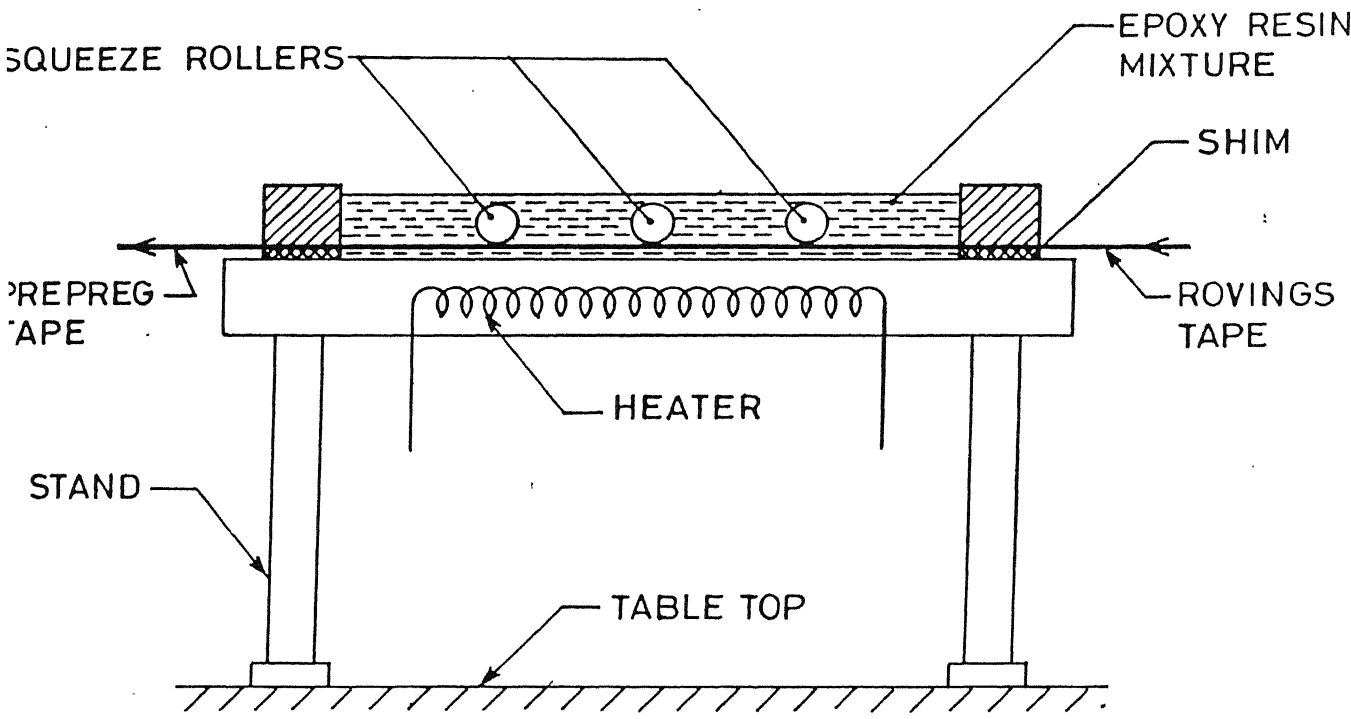
SQUEEZE ROLLERS

EPOXY RESIN
MIXTURE

SHIM

PREPREG
TAPE

ROVINGS
TAPE

HEATER

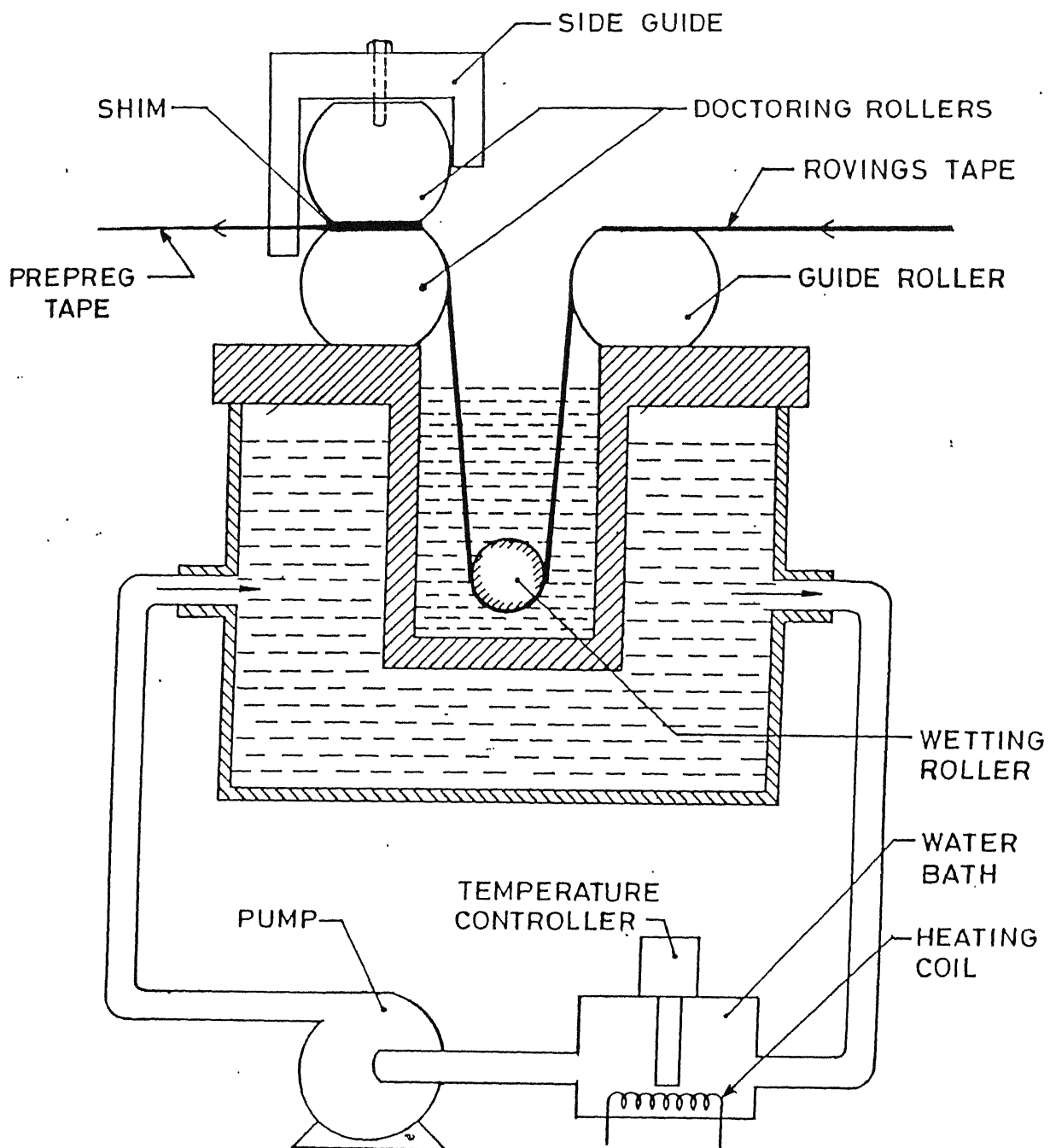STAND

TABLE TOP

FIG. 2.1   ORIGINAL RESIN BATH.

FIG. 2.2(a)   MODIFIED RESIN BATH.
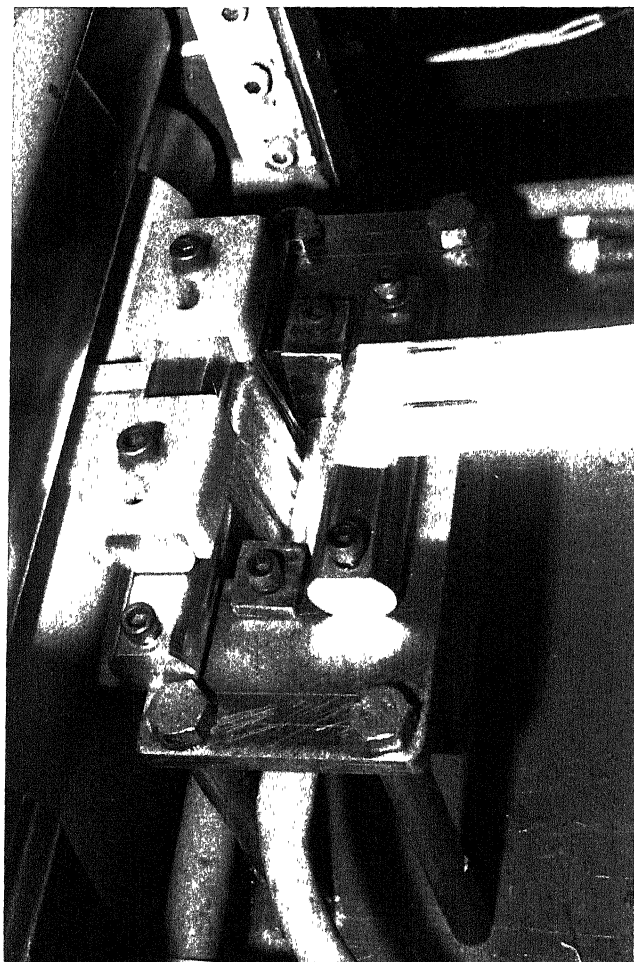
FIG. 2.2(b)   PHOTOGRAPH SHOWING MODIFIED RESIN BATH.

between resin bath and release film rollers to achieve superior wetting of fibers.

To avoid splitting of the fibre tape in lateral direction, after the wetted prepreg tape comes out of the doctoring rollers, provision has been made of prepreg side guides. These side guides, one on each side of the wetted prepreg tape are made of GFRP and are tightened to the top doctoring roller by a cap screw. Rotation of the side guides is constrained by the vertical walls touching the side of the top doctoring roller. The top surface of the side guides has a groove for lateral displacement along the axis of the doctoring roller.

The replenishment of epoxy resin mixture to the resin bath is carried out at a regular interval. Temperature of the new batch is maintained same as that of resin bath with the help of a temperature controller.

The advantages of modified design of resin bath are as follows:
. Enhanced wetting of fibers at considerably lower temperature of resin bath (55-60°C)
. No curing of epoxy resin mixture within the resin bath.
. Better control of the thickness of prepreg tape with packing shims between doctoring rollers.
. Uniform heating of resin bath.
. Reduced consumption of epoxy resin mixture during trial runs.
. Easy cleaning of resin bath on completion of run.

2.3 RELEASE FILM ROLLERS WITH HEATING ARRANGEMENT

As mentioned in chapter I, impregnation of fibers can be divided into two methods - impregnation via solution (e.g. Methyl ethyl ketone) and hot-melt technique. Though the impregnation of fibers is better in case of solution method, it poses the problem of solvent removal. Residual solvent causes voids in the resultant composite deteriorating its mechanical properties. However, a

trial run was conducted to analyse how the solution (methyl ethyl ketone) helps so far as wetting of fibers is concerned.

It was revealed that complete wetting of fibers takes place between the two release rollers owing to crashing of air bubbles. This enhanced wetting of fibers could be attributed to epoxy resin mixture built-up at the release film rollers, as shown schematically in Fig. 2.3(a). During trial runs without solution, it was noted that, the temperature of prepreg tape after it comes out of resin bath drops between resin bath and release film rollers leading to increase in viscosity of epoxy resin mixture. Consequently, the epoxy resin mixture built up at release film rollers does not take place and crashing of air bubbles is not effective anymore.

To restore the temperature of prepreg tape after it comes out of the resin bath, water bath heating arrangement has been provided to the release film rollers. As shown in Fig. 2.3(b), this consists of water bath with temperature controller, pump, distributor, collector, nozzle connections and rubber hose connections. The pump takes suction from water bath and supplies hot water to top and bottom release film rollers through distributor. On the other end, the collector collects water from top and bottom release film rollers and sends it back to water bath to form close loop heating cycle.

As shown in Fig 2.3(c),(d) the nozzle connection consists of Brass adaptor, Brass nozzle, supporting plate, spacer sleeves, rubber pad and distance piece. Adaptors are screwed to both the ends of top and bottom release film rollers to insert nozzles for inflow and outflow of hot water. The rubber hose connections from distributor and collector are connected to the nozzles, which are located in alignment with release rollers with the help of rubber packing and the distance piece. The supporting plate for nozzle is fitted to release rollers side covers with two screws and spacer sleeves. The Neoprene 'O' ring packing located in an

TOP RELEASE FILM

TOP RELEASE
FILM ROLLER

EPOXY RESIN MIXTURE
BUILT-UP

PREPREG TAPE

BOTTOM RELEASE
FILM ROLLER

BOTTOM RELEASE FILM
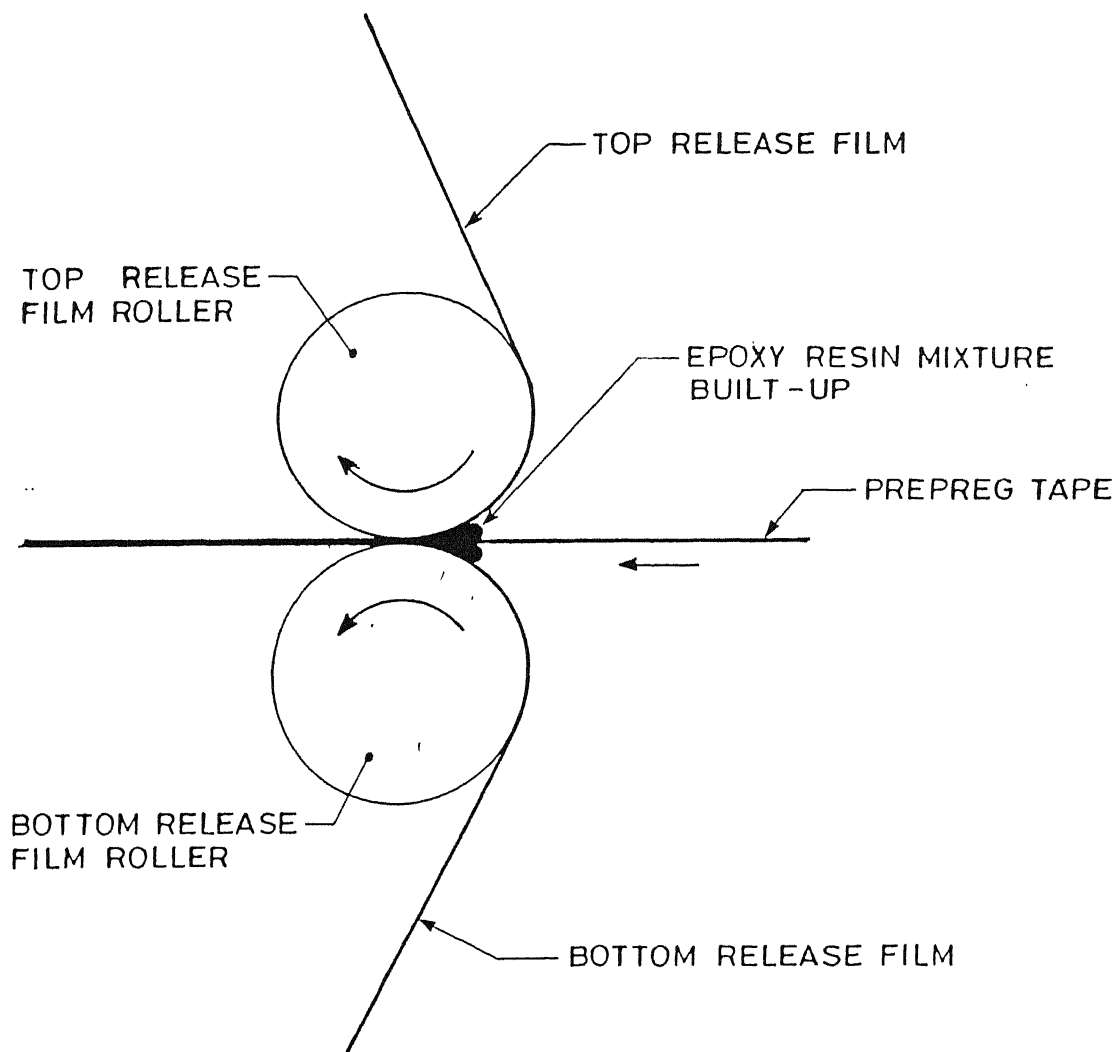
FIG. 2.3(a)   EPOXY RESIN BUILT-UP AT RELEASE FILM ROLLERS.

RELEASE FILM GUIDE

RUBBER HOSE

TOP RELEASE ROLLER

BOTTOM RELEASE ROLLER

RELEASE FILM GUIDE

TEMP. CONTROLLER

COLLECTOR

PUMP

DISTRIBUTOR

WATER BATH

HEATING COIL
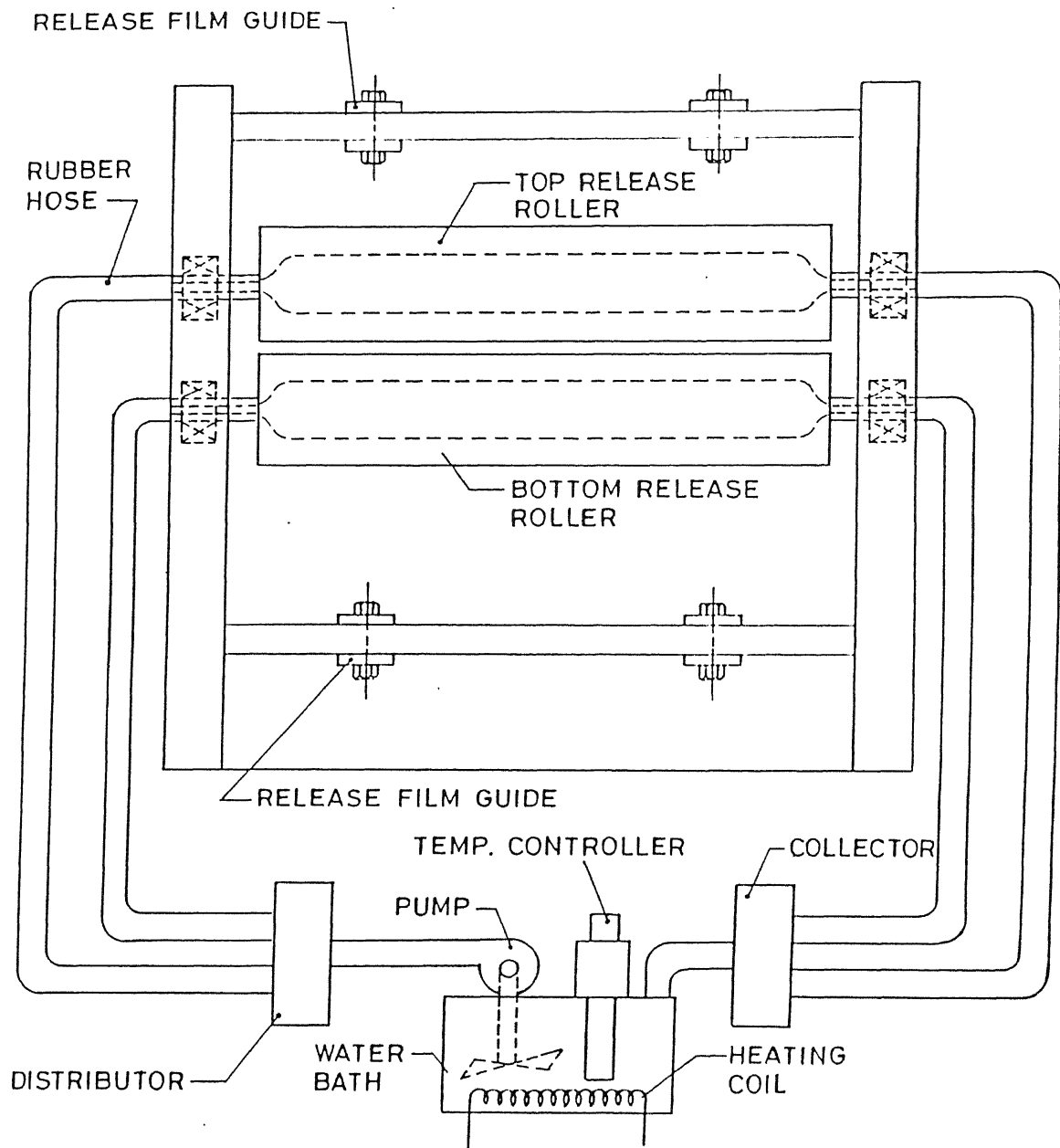
FIG. 2.3(b)   RELEASE FILM ROLLERS HEATING ARRANGEMENT.

FIG. 2.3(C)   PHOTOGRAPH   SHOWING   DETAILS   OF   NOZZLE
               CONNECTION   RELEASE FILM ROLLERS.
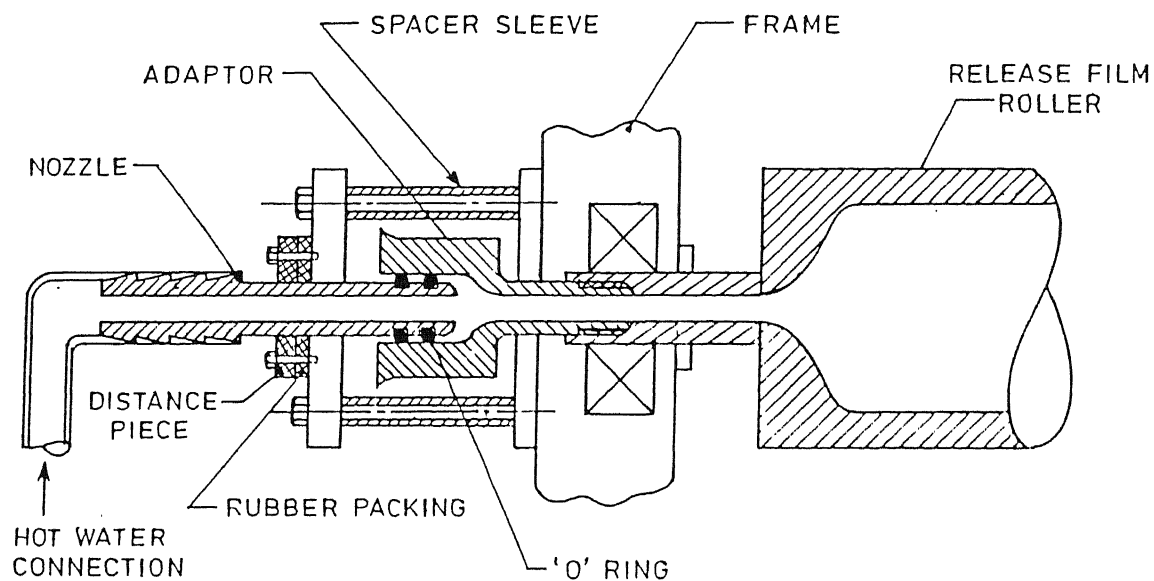
FIG. 2.3(d) SECTIONAL VIEW SHOWING DETAILS OF NOZZLE CONNECTION TO RELEASE FILM ROLLERS.

annular groove on the nozzle prevents leakage of water from nozzle and at the same time ensures smooth rotation of release rollers without increased friction. The annular groove size is decided in such a way that 10% diameteral compression of 'O' ring is obtained in the assembled state of the nozzle.

2.4 RELEASE FILM GUIDES :

As soon as, the prepreg tape comes out of the resin bath it is sandwiched between release films from either sides. There are two types of release films presently being used. The first type is BOPP (biaxially oriented polypropelene) film, which can be used up to the temperature of $100^{o}C$ of heating chamber. Above this temperature, the BOPP film shrinks in lateral direction. The second type of release film is silicone coated paper, which can be used at higher temperature (e.g. $140^{o}C$) of heating chamber. However, this paper was observed to be shifting sideways and hence getting damaged on the line, during trial runs.

To prevent this, a simple arrangement, as shown in Fig.2.4(a),(b), consisting of two GFRP strips, is fitted on the tie-rods of release film rollers assembly. The release film is restricted in lateral shifting by two sets of GFRP strips touching it from either sides. When the prepreg tape, covered with release films from top and bottom, comes out of the release film rollers, the films are stuck in their position and further guiding on the line is not essential.

2.5 ROVING STAND EYE-LIDS :

In the original layout of the machine, fibers were not guided properly as they come out of the cheese mount. This led to abrasion of fibers when they rub the edges of roving stand. Also, rovings tend to rub on each other when they were brought to form a tape. To minimize the friction, each roving is required to be

RELEASE FILM

TIE-RODS
OF FRAME
OF RELEASE
ROLLERS

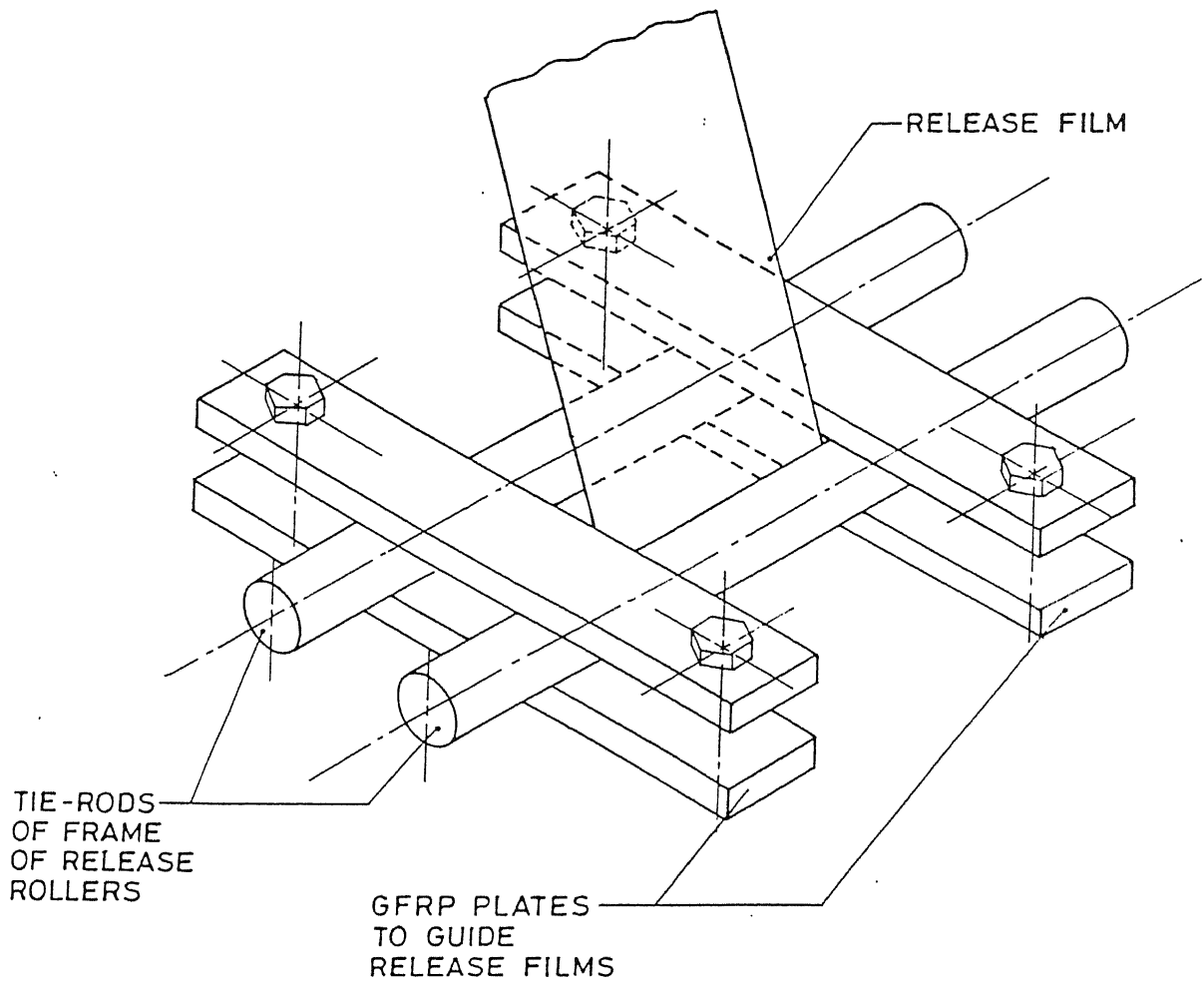GFRP PLATES
TO GUIDE
RELEASE FILMS
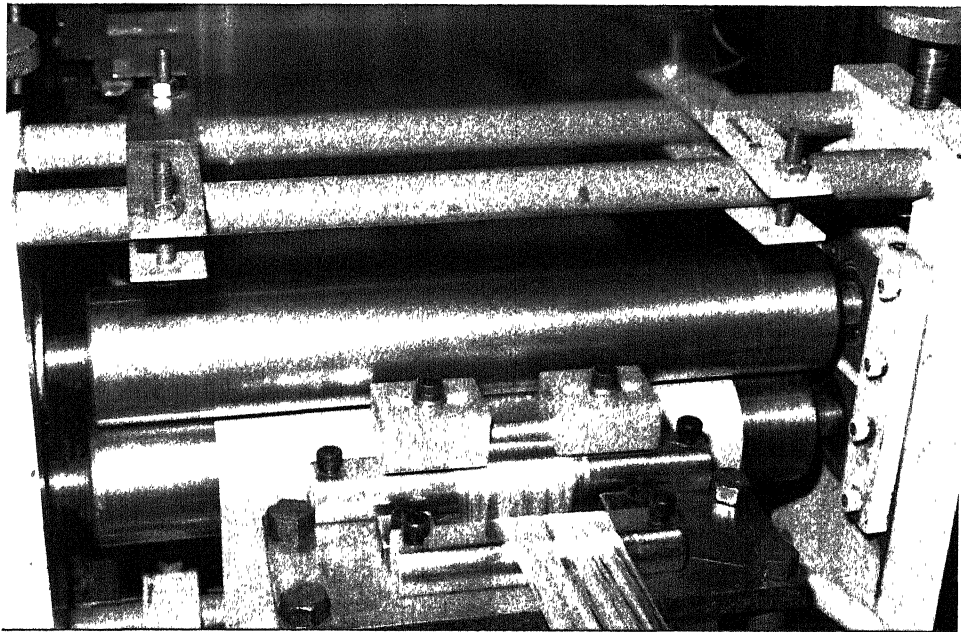
FIG. 2.4(a)   RELEASE FILM GUIDES.

FIG. 2.4(b)   PHOTOGRAPH SHOWING RELEASE FILM GUIDES.

passed smoothly through the eye-lids, before entering the collator. This is achieved with the help of eye-lids with flaired brass bush as shown in Fig.2.5(a),(b). The eye-lids subassembly is fitted at the front end of the roving stand.

2.6   INSULATION ON CHILLING PLATE :

When the semi-cured(B-staged) prepreg tape comes out of the heating chamber it remains still hot and will continue to advance in B-stage if it is not cooled immediately. The chilling plate consists of a curved aluminium upper surface plate, cooled due to flow of chilled water under the plate.

Due to accumulation of condensed water on the surfaces and sides of chilling plate, the following difficulties were posed :
. Friction between release film and top surface of chilling plate
   is increased resulting in tearing-off of the release film.
. The top plate of the main bed is corroded.
. The rubber clads of pulling rollers are likely to get damaged.

To minimise the condensation on the surfaces and sides of chilling plate, they are covered with insulating material(tharmocole).

2.7   SUMMARY

The performance of the machine is observed to be improved after carrying out the earlier mentioned modifications. The curing of epoxy resin mixture in the resin bath is eliminated during continuous run of the machine. The quality of the prepreg tape is superior owing to the complete wetting of fibers. The crashing of air bubbles in heated release film rollers enhanced the wetting of fibers. The release film is restricted in sideways shifting with the help of release film guides. The fitment of roving stand eye-lids considerably reduced the damage to fibers. The insulation on the chilling plate prevented condensation and hence

SECTION A A
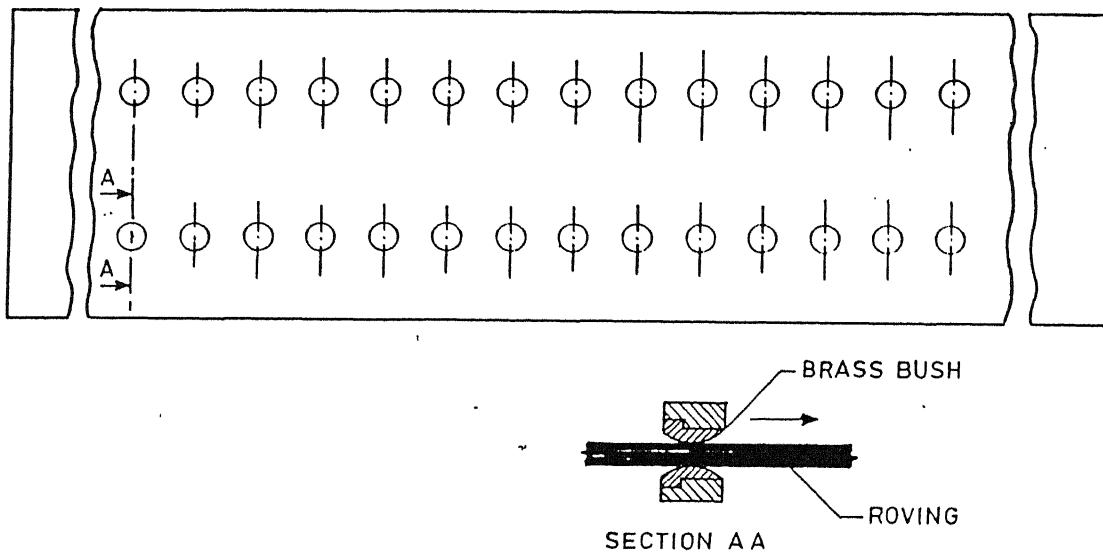
FIG. 2.5(a)   ROVING STAND EYE-LIDS SUBASSEMBLY.
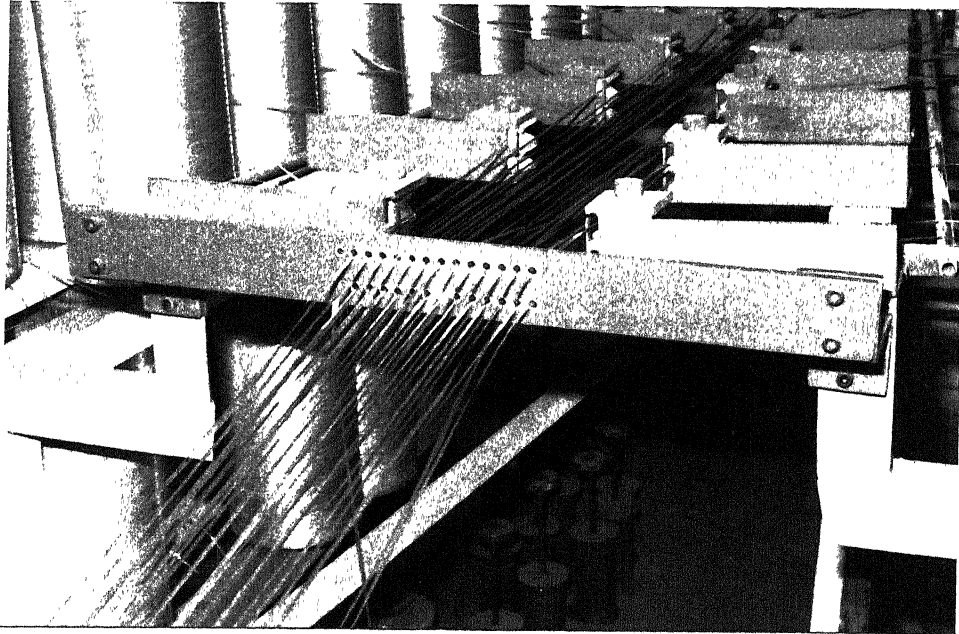
FIG. 2.5(b)   PHOTOGRAPH SHOWING ROVING STAND EYE-LIDS SUBASSEMBLY

the damage to release films and corrosion of top plate of main bed as well as damage to rubber clads of pulling rollers. The modified layout of the machine is schematically shown in Fig.2.6 (a),(b).
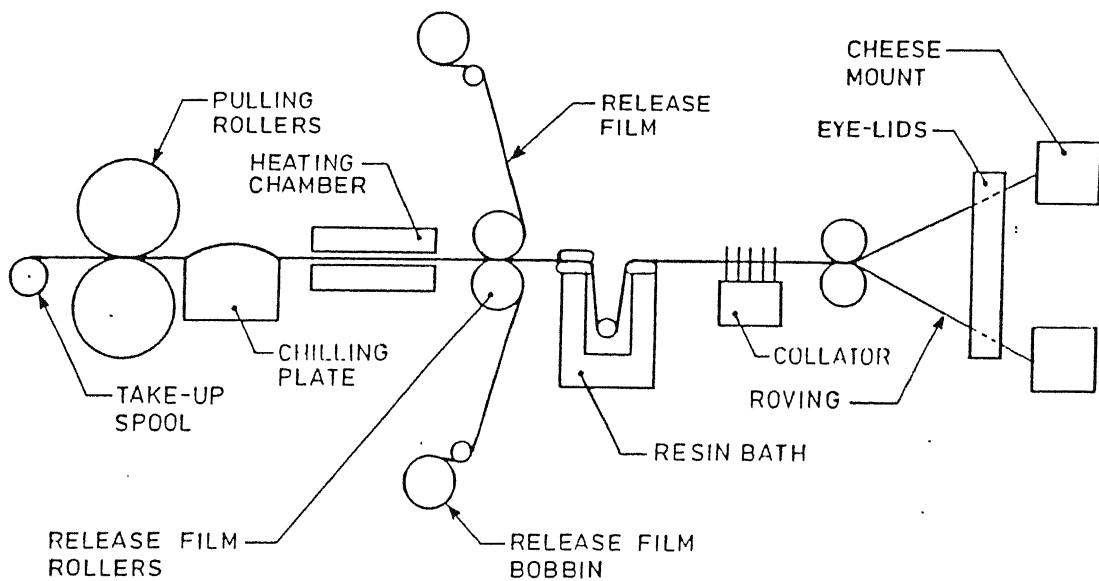
FIG. 2.6(a)   MODIFIED LAYOUT OF PREPREG MACHINE AT ESA LAB
MECHANICAL ENGG. DEPARTMENT, IIT KANPUR.
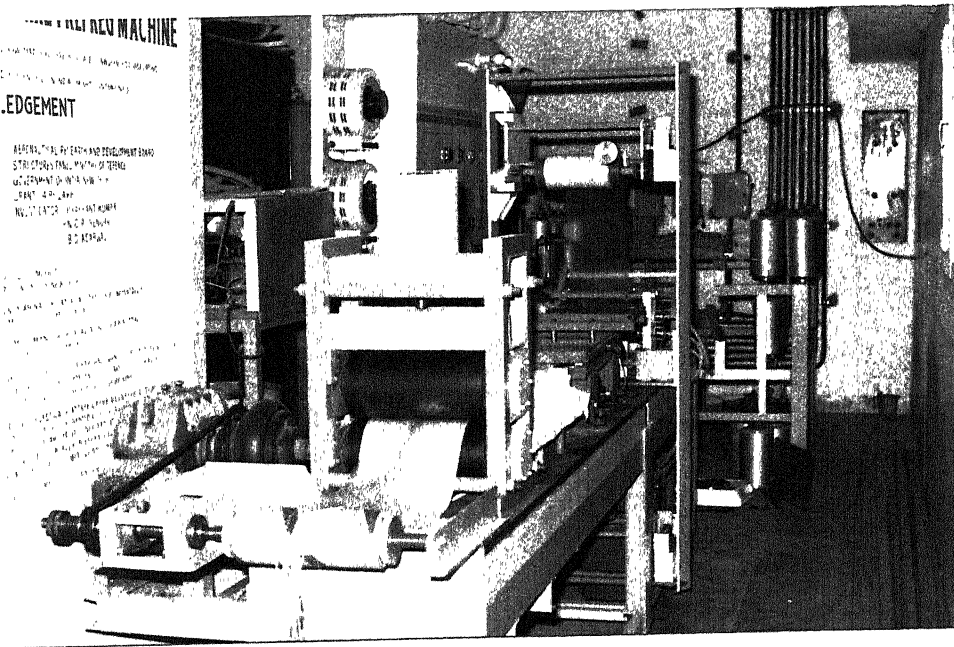
. 2.6(b)   PHOTOGRAPH SHOWING MODIFIED LAYOUT OF PREPREG
MACHINE   AT   ESA   LAB   MECHANICAL   ENGG.
DEPARTMENT   I I T KANPUR.

CHAPTER III

PREPREG PREPARATION AND CHARACTERIZATION

3.1 INTRODUCTION

Prepreg is either ready- to- mould material in sheet form or ready- to- wind material in roving form, which may be cloth, mat, unidirectional fiber or paper impregnated with resin and stored for use. The resin is partially cured to a B- stage and supplied to the fabricator who lays up the finished shape and completes the cure with heat and pressure [3].

On the broad scale, the preparation of prepregs consists of formulation of resin mixture and impregnation of fibers with resin mixture. As mentioned in chapter I, impregnation of fibers can be carried out by several methods. (i)impregnation via solution in which solution is added to resin mixture to obtain desired viscosity . (ii) Hot-melt technique in which the temperature of the resin mixture is controlled to maintain its viscosity. The two methods are compared for their relative advantages and disadvantages in Table 3.1.

TABLE 3.1 Comparison of impregnation via solution and hot-mel technique.

Impregnation via solution	Hot-melt technique
. Impregnation can be carried out without applying high pressure, which minimizes fiber damage.	. Impregnation with doctoring system can cause damage to fibers.
. Tackiness also depends on amount of residual solvent present.	. Uniform tackiness better for automated production is det- mined by resin system alone.

- Residual solvent deteriorates laminate properties.

- Void content is small.

- Environmental problems from possible solvent emission.

- Not applicable because solvent is not used.

Since, the hot- melt technique does not pose the problem of solvent removal it has been preferred in the present work.

This chapter covers description of various types of thermosetting resins in general and epoxy resins in particular. Formulation of epoxy resin mixture is explained in detail alongwith their chemical formulae. The various steps involved in the preparation of prepregs and their characterization is stated. The chapter has been concluded by taking into consideration the results obtained during characterization.

3.2 TYPES OF THERMOSETTING RESINS

The most convenient and widely used matrices are thermosetting resins. Easy processibility and good chemical resistance are their chief advantages [6]. They have cross- linked structure with covalent bonds between all the molecules. Once cured they do not soften, but decompose on heating. There are various types of thermosetting resins such as epoxies, unsaturated polyesters and polyimides.

3.2.1 Epoxy Resins

Epoxy resins [6,7] are low molecular weight organic liquids containing a number of epoxide groups situated internally, terminally or on cyclic structures capable of being converted into useful thermoset form.
In a broad sense, the term epoxide refers to a chemical group consisting of an oxygen atom bonded with two carbon atoms already

united in some other way as shown in Fig.3.1
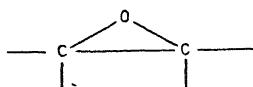
Fig. 3.1 Epoxide group

Ethylene oxide is the simplest epoxy to which the term α- epoxy or 1,2 epoxy is applied.

Basic characteristics of epoxy resins

. Low viscosity: The liquid resins and their curing agents form low viscosity, easy to process systems.

. Easy cure: Epoxy resins cure quickly and easily at any temperature from 5 to 150°C, depending on the selection of curing agent.

. Low shrinkage: The most advantageous property of the epoxy resins is their low shrinkage during cure. Epoxy resins react with very little rearrangement and no volatile by- products are evolved.

. High adhesive strength: Owing to the presence of polar hydroxyl and ether groups, the epoxy resins are excellent adhesives.

. High mechanical properties: The strength of properly formulated epoxy resins is high as a result of their low shrinkage, which minimizes stresses that otherwise would weaken the mechanical structure.

. Versatility: The basic properties can be modified in many ways by blending of resin types, by selection of curing agents and by use of modifiers and fillers [6].

The most common process for producing epoxies is epoxidation which is the introduction of the three- membered ring into an organic compound. The various types of epoxidation of unsaturated hydrocarbons are [7]

. Catalytic oxidation
. Epoxidation by organic and inorganic peroxy acids and their derivatives
. Epoxidation via halohydrin
. Biological epoxidation.

3.2.2 Polyester resins

A polyester resin [1,2,8] is an unsaturated (reactive) polyester solid dissolved in a polymerizable monomer such as styrene. They have long chain of linear polymers containing a number of carbon double bonds. A typical polyester resin made from reaction of maleic acid and diethylene glycol is shown in Fig.3.2

Maleic acid   Diethylene glycol
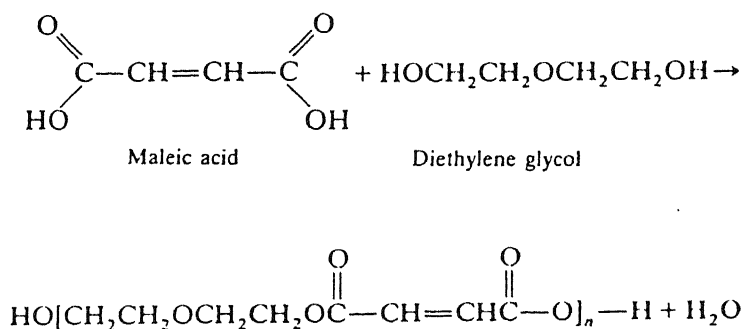
Fig. 3.2 Polyester resin

The curing takes place by addition of curing agent and is initiated by a free radical mechanism . This is an exothermic reaction leading to shrinkage. The properties of base resin can be altered by changing the nature and ratios of raw materials.

3.2.3 Polyimides

Polyimides [9] are a polymer produced by heating of polyamic acid. They can be used up to a temperature of 300°C. Usually, polyimide precursors are produced for impregnation of fibers which are subsequently cured by heating. Two classes of precursors are (i) curable by condensation reaction and (ii) by addition reaction. An example of polyimide molecule is shown in Fig.3.3.
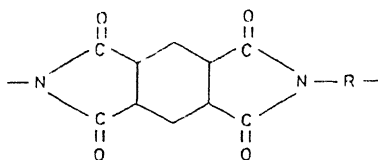
Fig. 3.3 Polyimide molecule

3.3 FORMULATION OF EPOXY RESIN MIXTURE

The impregnating solution used has the following composition.

ARALDITE LY 556	100 parts by weight
Hardener HT 976	35 parts by weight
Accelerator XY 73	2 parts by weight
γ - Amino propyl triethoxy silane	0.5 parts by weight

3.3.1   ARALDITE LY 556

This is a liquid unmodified diglycidyl ether of bi-sphenol A epoxy resin [9,10].   Fig.3.4 shows the chemical structure of diglycidyl ether of bisphenol A [6].
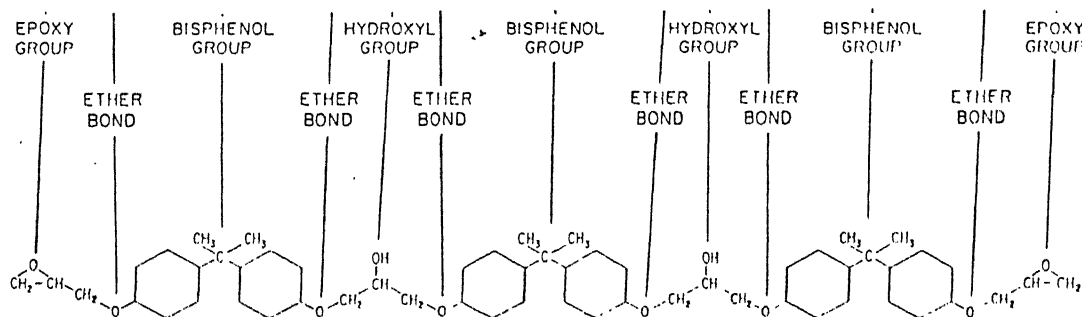
Fig. 3.4 Chemical structure of diglycidyl ether of bi-sphenol A epoxy resin

3.3.2 Hardener HT 976

Hardener is a substance added to basic resin to promote or control curing action by taking part in it. Hardener HT 976 is Diaminodiphenyl sulphone (DDS) [9,10].

It is an aromatic amine defined as one in which the amine nitrogen is attached directly to an aromatic ring such as shown in Fig.3.5.
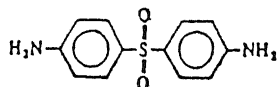
Fig. 3.5 Chemical structure of Diaminodiphenyl sulphone

Aromatic amines are generally solids at room temperature. They are converted into liquid form by various techniques such as melting, eutectic blending, adduct formation and modifying with diluents [6].

3.3.3 Accelerator HT 973 or XY 73

Accelerator is a substance which is added to a mixture of resin and hardener to speed up the curing reaction.

HT 973 is Boron trifluoride Mono ethylene Amine (BF$_3$- MEA) [9,10] with chemical structure as shown in Fig. 3.6.

$$F-B:NH_2-CH_2-CH_3$$

with F atoms bonded to B above and below.
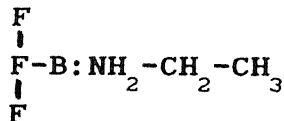
Fig. 3.6 Chemical structure of Boron trifluoride mono ethylene amine.

With the glycidyl ether resins(DGEBA) the reaction of HT 976 (DDS) is sluggish, therefore phenols and boron trifluoride complexes are normally used [6]. However, XY 73 should not be used as lone curing agent because it results in brittle matrix.

3.3.4 Silane coupling

The chemical treatments applied during the forming of glass fibers are called sizes. There are two types - temporary sizes and compatible sizes. The temporary sizes are applied to minimize the degradation of strength resulting from abrasion of fibers to one another. The compatible sizes are applied to help improve initial adhesion of resin to glass and to reduce the destructive effects of water and other environmental forces on this bond [2].

The compatible sizes are called coupling agents such as organofunctional silanes. They have chemical formula as follows :

$$X_3 \; Si \; (CH_2)_n \; Y$$
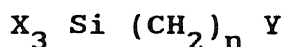
Where n = 0-3

     Y = organofunctional group that is compatible with polymer matrix

     X = hydrolyzable group on silicon

γ - amino propyl triethoxy silane has the structure as shown in Fig. 4.7.

$$H_2 \; N \; CH_2 \; CH_2 \; CH_2 \; Si \; (OC_2 \; H_5)_3$$
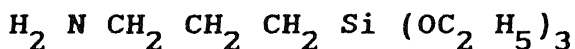
Fig. 4.7 Chemical structure of γ- amino propel triethoxy silane

The manufacturers of fibers carry out the application of compatible sizes to glass fibers from 0.1 to 0.5% of the weight of glass treated. However, to counter for any discrepancies in their application during glass fiber manufacturing, it has been recommended to add 0.5% of silane coupling to epoxy resin mixture [10].

3.4 PREPARATION OF PREPREGS

In the hot-melt technique, the preparation of prepregs commences with collation of rovings to form tape at collator followed by their impregnation in the resin bath (Fig.2.6(a)) maintained at the temperature of 55-60°C. The release films are applied from either sides of prepreg tape. The gap between the heated release film rollers is adjusted so as to achieve hot compaction of the prepreg tape. The next operation on the line is partial curring (B-staging) which is an intermediate stage in the reaction of thermosetting resins such that the resin swells when in contact with certain liquids and softens when heated but may not entirely dissolve or fuse [1]. This process is carried out during the passage of prepreg tape through heating chamber maintained at a temperature of 120-130°C. The prepreg tape should remain inside the heating chamber for approximately 5-10 minutes. To arrest further curing, prepreg tape is passed over chilling plate maintained at 2 - 5 ^{O}C and is finally wound on a take-up spool.

3.5 PREPREG CHARACTERIZATION

3.5.1 Introduction

The experimental characterization of the prepreg is essential so as to evaluate the performance of the machine after each modification was carried out. The quality of prepreg tape is judged taking into account the following characteristics.

. Tack : Stickiness of reinforced resin prepreg material [1].
. Drape : The ability of prepreg tape to confirm to an irregular shape [1].
. Gel time : The stage at which a liquid begins to exhibit pseudo-elastic properties[1].

The prepregs have been characterized to determine the extent of wetting by visual inspection and resin content is determined by

burn test as well as by analytical method, as described in the following sections.

3.5.2 Visual inspection

The extent of wetting of fibers can be determined by observing the transparency of the prepreg tape by naked eye. Uniform wetting of fibers is reflected by excellent transparency of the prepreg tape.

3.5.3 Resin content

The resin content is determined by two methods - burn test and analytical method as mentioned in the following sections.

Burn test

The prepreg tape specimen is weighed in air and in water with the help of weighing machine and specially designed stand, described in section 5.3.1. The specimen is then placed in a furnace maintained at a temperature of $750-800^{O}C$ until all evidence of resin is absent. The ignition residue is cooled and weighed to find weight of fibers [11].

Percentage weight fraction of fibers is given by,

$$W_f = (w_f / w_{pa}) \quad 100$$

where w_f = weight of fibers and w_{pa} = weight of prepreg in air. Similarly, percentage weight fraction of resin becomes,

$$W_m = [(w_{pa} - w_f) / w_{pa}] \quad 100$$

Density of prepreg tape can be found by expression,

$$\rho_p = (w_{pa} / w_{pa} - w_{pw})$$

where w_{pw} = weight of prepreg in water.

Knowing the density of fibers (ρ_f = 2540 kg/m^3) [2], volume fraction of fibers is given by,

$$V_f = (\ W_f\ \rho_p\ /\ \rho_f)\quad 100$$

and percentage volume fraction of resin is given by,

$$V_m = 100 - V_f$$

Table 3.2 gives the results of resin content determination by burn test.

TABLE 3.2 Resin content in prepreg as determined by burn test.

Sr. No.	w_{pa} gm	w_{pw} gm	ρ_p gm/cc	w_f gm	w_m gm	W_f %	W_m %	V_f %	V_m %
1.	0.202	0.101	1.998	0.150	0.052	74.1	25.9	58.3	41.7
2.	0.208	0.498	1.701	0.889	0.319	73.6	26.4	49.3	50.7
3.	1.248	0.644	1.653	0.831	0.417	66.6	33.4	54.1	45.9
4.	0.876	0.408	1.870	0.637	0.239	72.7	27.3	53.6	46.4
5.	1.123	0.534	1.905	0.822	0.301	73.2	26.8	54.9	45.1

Analytical method

This method enables to calculate the resin content by measuring the dimensions (width, thickness) of the prepreg tape.

Cross-sectional area of prepreg tape with width w and thickness t is, A = w t. Percentage volume fraction of fibers is given by,

$$V_f = \frac{(Tex/1000)\,N}{A\ \rho_f}$$

Because, Tex gives the weight in grams of fiber roving of 1000m in

length. The weight of fibers per meter length of tape is $\frac{Tex\ N}{1000}$

in grams, where N is fiber ends used in the prepreg. Then the volume of the fibers in the tape becomes $\frac{Tex\ N}{1000\ \rho_f}$ where ρ_f is the

density of glass fibers (2540 kg/m^3 [2]) The volume fraction of fibers in the prepreg is given by,

$$V_f = \left(\frac{Tex\ N}{1000\ \rho_f}\right) / A$$

Table 3.3 gives the results of resin content determination by analytical method for glass fiber Tex = 600.

TABLE 3.3 Details of prepreg dimensions and volume fractions by analytical method.

Sr.no	N	w (mm)	t (mm)	A (mm^2)	V_f (%)	V_m (%)
1.	24	46	0.240	11.04	51.35	48.65
2.	26	53	0.240	12.72	55.63	44.37
3.	27	54	0.230	12.42	51.35	48.65
4.	28	60	0.225	13.50	48.99	51.01
5.	28	54	0.235	12.69	52.12	47.88
6.	26	51	0.200	10.20	60.21	39.79

Table 3.4 compares the resin content of prepreg as determine through the two methods.

TABLE 3.4 Volume fractions as determined through burn test and analytical method.

Sl. No.	Specimen No.	V_m by Burn Test	V_m by analytical method
1.	22/94	41.7	51.01
2.	23/94	50.7	47.88
3.	01/95	46.4	48.65
4.	03/95	45.9	50.55
5.	06/95	45.1	39.79

3.5.4 Flow testing

The flow test is conducted to determine how the resin will flow during subsequent laminating operation. It is desirable that the flow be sufficient to produce uniform wetting of fibers and not so great that resin flows out during curing and results into resin starved portions of the laminate.

Following the procedure of flow testing [11], two plies of prepreg tape (50mm x 50mm) are stacked and weighed (initial weight). The stack is placed between the platens of a press with parting films (Teflon coated glass fabric) applied from either sides. The press is maintained at a temperature of $121^{\circ}C$ and a pressure of 0.7 Mpa. The duration inside the press is 15 minutes or until the resin has gelled. On completion of curing the stack is reweighed after removing parting films (final weight).

Percentage flow is given by,
 (Initial weight - final weight / Initial weight) 100

This test has been carried out for one specimen to obtain percentage flow as 6.59%.

3.6 CONCLUSION

It has been concluded that, using only indigenous raw materials and following the hot-melt technique, prepregs of good quality, with fiber volume fraction between 50% to 60%, have been prepared.

CHAPTER IV

PREPREGS TO ENHANCE INTERLAMINAR FRACTURE TOUGHNESS

4.1 INTRODUCTION

Interlaminar fracture toughness of polymer composites is an important parameter, because laminates are susceptible to delamination failure [12]. In order to enhance their fracture toughness, toughened matrices using elastomeric modifiers have been explored for last two decades [4]. The modification of thermosetting matrix composites by adding rubber or thermoplastics or a ductile material to the matrix, can be carried out by several different techniques [13]. Such as:

. Rubber toughening
. Mixing a thermoplastic resin with thermosetting resin
. Coating the fibers with an elastomer, thermoplastic or a ductile material
. Interleaving the laminae of fiber reinforced resin with thin film of a ductile thermoplastic or toughened thermosetting resin

In this chapter, a preliminary work to enhance the interlaminar fracture toughness of the laminate, is presented. Laminates of glass/epoxy are fabricated by modifying epoxy resin mixture with carboxyl terminated butadiene-acrylonitrile (CTBN polymers). The technique is based on the mechanism of rubber toughening.

4.2 FORMULATION OF MODIFIED EPOXY RESIN MIXTURE

4.2.1 Rubber toughning:

The basic principal is that the brittle thermosetting resin can be made tough and ductile by addition of a suitable rubber. The

rubber is dispersed in small spheres of the order of 1 μm in diameter in resin. To produce rubber dispersion, the rubber is first dissolved in liquid resin and then is precipitated during cross-linking of the polymer. Therefore, the dissolution of rubber in the resin is a necessary condition in this approach. The rubber used with epoxy polymer is carboxyl terminated butadiene-acrylonitrile (CTBN) polymer. There are three types of reactive functional groups commercially available.They are carboxyl, acrylate vinyl and secondary amine. The following is a key to nomenclature [10]

C : Carboxyl.
V : Vinyl.
A : Amine.
T : Terminal reactive groups.
B : Butadiene.
N : Acrylonitrile.
X : Pendent reactive groups.

The carboxyl group of the rubber reacts with the epoxy group of the resin to form a block polymer. This reaction is best accomplished before adding hardener, otherwise the hardener completes with the carboxyl groups. The molecular weight of the CTBN polymer is approximately ten times that of epoxy resin. The choice of CTBN polymers will depend on the required compatibility and functionality. In general, the compatibility of CTBN polymer with the diglycidyl ether of bi-sphenol - A (DGEBA) type epoxies increases with increasing acrylonitrile concentration. The optimum toughening effect is generally obtained within a range of acrylonitrile content from 12 % to 18 % of epoxy resin [15].

4.2.2 Preparation of the modified epoxy resin mixture:

The modified epoxy resin mixture used has the following composition:

ARALDITE	LY 556	100 parts by weight
Hardener	HT 976	35 parts by weight
Hardener	HT 973	2 parts by weight
γ-Amino propyl tri ethoxy silane		0.5 parts by weight
CTBN	1300 X 8	15 parts by weight

The first part of the mixture is prepared in which 50 parts by weight of LY 556 is heated to 130°C and 7.5 parts by weight of CTBN is dissolved in the hot resin. The second part of the mixture is similarly prepared in another pot so as to finally obtain 100 parts by weight of LY 556 and 15 parts by weight of CTBN polymer. The hardener HT 976 is dissolved in the hot resin kept in first pot with thorough stirring. The mixture is then allowed to cool to 100°C and the hardener HT 973 is dissolved in it. As soon as HT 973 is completely dissolved, the second part kept ready in another pot is added. This is followed by addition of 0.5 parts by weight of silane coupling.

Impregnation of glass fibers has been carried out with modified epoxy mixture (with 15 parts by weight of CTBN) as well as with unmodified epoxy resin mixture (without CTBN) in two different runs of the prepreg machine to make two different types of prepregs. However, the running parameters of the prepreg machine were kept constant for both the runs.

4.2.3 Laminate preparation

Two sets of laminate, one by using prepregs without CTBN and the other by using prepregs with 15 parts by weight of CTBN, were prepared under the identical curing and post-curing conditions as stated below:

For curing

Press temperature	150°C
Pressure	0.7 MPa
Duration	180 minutes

For post-curing

Temperature	180°C
Duration	120 minutes

4.3 IMPACT INDUCED DAMAGE TOLERANCE COMPARISON

The experiment of impacting projectile on laminates using air gun assembly simulates damage caused by runway debris to aircraft components [12].

Both the sets of laminate were impacted with the help of an air gun assembly at different velocities. The size of each laminate was 120 × 120 mm. The hemispherical mild steel projectile (weight 11.84 g) was used. The velocity of the projectile was measured through an optical system. The details of the air gun impact facility are given elsewhere [12].

The visual comparison of impact induced damage area as well as damage area measurement using planimeter has been carried out. Table.4.1 gives the values of velocity of projectile and corresponding impact induced damage area on laminates without CTBN and Table 4.2 on laminates with CTBN.

Table 4.1 With CTBN

Specimen No.	Velocity m/s	Damage area sq.cm
B 1	48.4	4.0
B 2	57.1	6.2
B 3	70.7	10.5
B 4	78.0	13.5

Table 4.2 Without CTBN

Specimen No.	Velocity m/s	Damage area sq.cm
A 1	49.1	4.3
A 2	57.3	6.0
B 3	70.2	11.5
B 4	77.8	13.5

4.4 DISCUSSION AND RECOMMENDATIONS

The comparison of the impact induced damage area of laminates with modified epoxy resin mixture (with 15 parts by weight CTBN) and with unmodified epoxy resin mixture (without CTBN), revealed that there has not been any significant improvement in the impact induced damage. However, because of the negative results further investigation was discontinued and no attempt was made to determine interlaminar fracture toughness of these laminates. The toughening of matrices is not effectively transferred to the laminates may be because rubber precipitation does not take place at the interface. It is expected that through the thickness fracture toughness of laminates may increase by modification of epoxy resin mixture with CTBN.

Owing to the availability of prepreg making machine to prepare cross-ply laminates, it was possible to undertake this work. It is pertinent to mention that such type of work was not possible so far, because laminate through hand lay-up technique using unidirectional fabric is not the way laminates are made in industry.

It is suggested that further investigation can be undertaken to modify the epoxy resin mixture such that rubber dispersion takes place only during final curing. Also, tests can be carried out to determine through the thickness fracture toughness of modified epoxy resin mixture laminates.

CHAPTER V

LAMINATE PREPARATION AND CHARACTERIZATION

5.1 INTRODUCTION

Fabrication of fibrous composites can be broadly classified as wet forming processes and processes using premixes or prepregs [2]. As mentioned in chapter II, the wet forming process consists of combining fibers and matrix together and curing is competed in one step. In the dry forming process, forming and moulding operations are uncoupled. The first step is to prepare prepregs which are used during second step to prepare laminate. Hand lay-up which means the placement of layer after layer of a tape in a prescribed orientation, is followed for laminate preparation.

The laminates prepared through the prepregs are required to be tested to determine the suitability of the processes and to evaluate the quality of the prepreg tape. The characterization of laminates [14,13] has been carried out to determine fiber volume fraction, tensile strength and modules, compressive strength, interlaminar fracture toughness and through the thickness fracture toughness.

This chapter deals with laminate preparation to describe the steps involved in the process and characterization of laminates to determine the above mentioned properties. Results of the various tests are listed at the end of each section alongwith conclusions.

5.2 LAMINATE PREPARATION

The laminate preparation commences with stacking of individual plies with orientation as $[(0/90)_4]_s$. The resultant laminate is called cross-ply laminate [2]. For preparing the stack by hand lay-up technique, first parting film (teflon-coated glass fabric)

is placed on a flat plate. The prepreg tapes are then stacked on it as per the orientation mentioned above. The stacking is covered from top with another parting film of teflon coated glass fabric and is reamed over by a steel rod to remove all air pockets and wrinkles. Felt strips are placed at the four edges of the stacking to absorb squeezed out epoxy during curing. The compressed thickness of felt strips should be less than 2.5 mm. The entire assembly is then placed between the two platens of the hydraulic press, as shown in Fig. 5.1.

5.2.1 Pre-curing cycle

Prepreg tape prepared in the machine is not obtained in proper B-stage, because duration for which the prepreg tape should remain inside the heating chamber is 5-10 minutes. Owing to this, at high temperature and pressure the viscosity of resin mixture decreases so much that, a large portion of resin mixture flows out from the stacking of prepregs. This results in resin starved portions in resultant laminate. To avoid this, curing is carried out in two steps (i) pre-curing to bring stacking to a B-stage and (ii) final curing.

To accomplish the pre-curing, the stacking is required to be kept in the platens of hydraulic press at a temperature of $120-130^{\circ}C$ without pressure for approximately 100-110 minutes to obtain the epoxy resin mixture in gel stage. In this stage, the epoxy resin mixture does not flow out of the plies, hence resin starved portions are not observed in the resultant laminate. The pre-curing cycle temperature and duration has been determined in a separate experiment. A small quantity of resin mixture was heated under controlled conditions at temperature range of $100-130^{\circ}C$ and its viscosity variation was monitored over the period of time.

5.2.2 Curing cycle

On completion of pre-curing cycle, the laminate stacking is cured for 4 hrs at a pressure of 0.7 MPa and a temperature of $130^{\circ}c$ [16]

TOP PLATEN

HEATING COIL

TEFLON COATED
GLASS FABRIC
(PARTING FILMS)

FELT

STACK OF
PREPREGS

SPHERICAL STEEL BALL
FOR IMPARTING POINT
LOAD
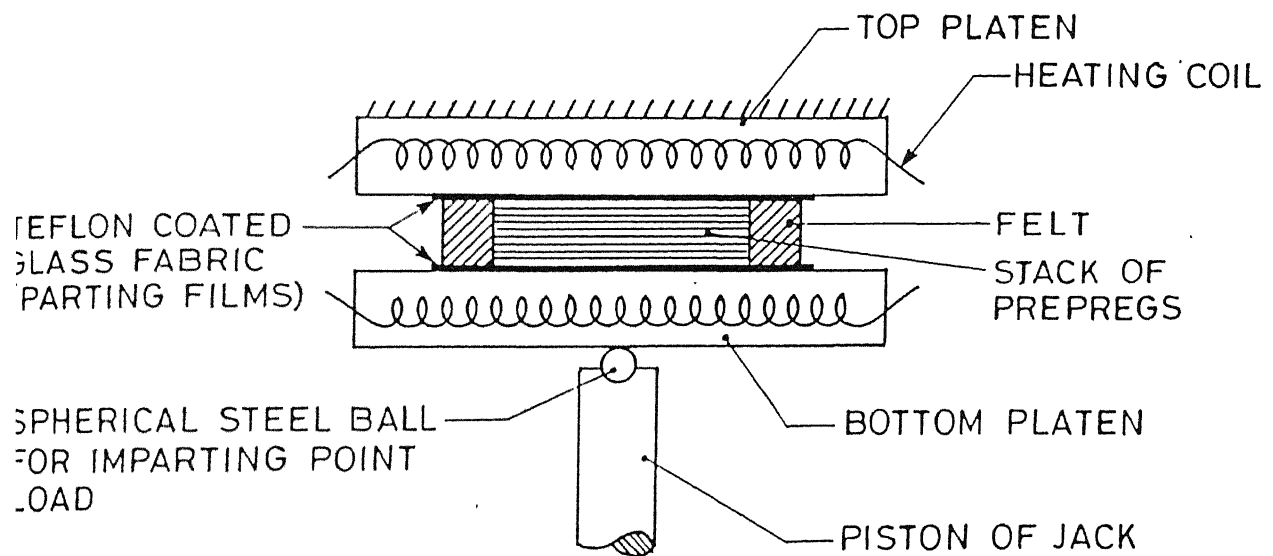
BOTTOM PLATEN

PISTON OF JACK

FIG. 5.1   ARRANGEMENT OF CURING A STACKING OF PREPREG
BETWEEN THE TWO HEATED PLATENS OF A HYDRAULIC
PRESS, SHOWING FIXED TOP PLATEN AND THE POINT
LOAD IS APPLIED TO THE BOTTOM PLATEN WITH THE
HELP OF A STEEL BALL.

in the same assembly as shown in Fig. 5.1. It is advisable to [
the laminate stacking under pressure in stages of 0.1 Mpa [
minute. Laminates of higher quality will be obtained if they a
allowed to cool carefully and slowly, at full laminating pressur
from 130°C to 100°C [16].

5.2.3 Post-curing cycle

The laminate stacking is removed from the hydraulic press aft
curing and is placed for post-curing in the heating chaml
maintained at a temperature of 150°C for 8 hours without pressu
[15].

5.3 CHARACTERIZATION OF LAMINATES

The fabrication process influences the properties of polym
composites. It is well known that, the curing cycle,and tooli
influence to a large extent the basic properties and hence t
quality of the product. In order to standardize the produ
properly, it is essential that characterization is undertaken
each stage during the development of the machine. The te
requirements for physical and mechanical properties determinati
have been standardized by ASTM [13,17].

The following sections describe the specimen geometry a
experimental technique to determine fiber volume fraction, tensi
strength and modules, compressive strength, interlaminar fractu
toughness and through the thickness fracture toughness of t
laminates made through the prepregs prepared as mentioned
chapter III.

5.3.1 Fiber volume fraction

The most important factor determining the properties of polym
composites is the relative proportions of the matrix and fibe
The relative proportions can be given as the weight fractions

the volume fractions as follows [2]:

Weight fraction of fibers (W_f) and matrix (W_m) is given by,

$$W_f = w_f/w_c$$

$$W_m = w_m/w_c$$

where, w_f = weight of fiber

w_m = weight of matrix

w_c = weight of composite material

To find volume fractions from weight fractions, the density ρ_c, of the composite material must be obtained. The conversion between the weight fraction and volume fractions can be obtained by the following expression:

$$V_f = (\rho_c/\rho_f) \quad w_f$$

$$V_m = (\rho_c/\rho_m) \quad W_m$$

where, V_f and V_m are fiber and matrix volume fractions while ρ_c ρ_f and ρ_m are densities of composite, fiber and matrix respectively.

The burn test is adopted, in this study to determine fiber volume fraction. In this method, the specimen of laminate (approximately of area 25 mm x 25 mm) is weighed in air (w_{ca}) on a weighing machine capable of measuring weight with the accuracy of 0.0001gm To determine the density of the composite it is necessary to find the weight of the same specimen in water (w_{cw}). This is obtained with the help of specially designed stand as shown in Fig 5.2 Thus, the density of composite can be obtained as follows:

$$\rho_c = w_{ca}/ (w_{ca} - w_{cw})$$

The specimen is then placed in a furnace at a temperature of 75

FIG. 5.2   PHOTOGRAPH SHOWING A WEIGHING MACHINE WITH
SPECIALLY DESIGNED STAND TO DETERMINE WEIGHT
OF SPECIMEN IN WATER.

to 800°c for 2-3 hrs or until the matrix is burnt out. The ignition residue is cooled and reweighed to obtain weight of fibers, w_f. The fiber weight fraction and hence volume faction can be determine as described earlier. This test has been carried out as a routine matter, however some of the results are listed in Table 5.1

TABLE 5.1 Results of fiber volume fraction determined by burn test.

Sl. No.	Lamin--ate No	w_f (gm)	w_m (gm)	W_f (%)	W_m (%)	V_f (%)	V_m (%)
1.	32/94	3.0478	0.8603	77.98	22.01	62.69	37.31
2.	34/94	3.3878	1.0696	76.00	24.00	60.29	39.71
3.	39/94	2.2462	0.7135	75.89	24.10	63.50	36.50
4.	41/94*	2.7310	1.0438	72.34	27.65	55.64	44.36
5.	01/95*	2.0682	0.792	72.30	27.69	52.82	47.18
6.	06/95	0.9777	0.3226	75.18	24.82	58.24	41.76

* Resin-starved laminates.

As listed in Table 5.1, the fiber volume fraction of the laminate prepared through prepregs is approximately 60%. It is observed that if the fiber volume fraction increases further (e.g. 70%), the resultant laminate shows resin starved portions. Therefore, it is concluded that the fiber volume fraction close to 60% in conjunction with enhanced transparency of the laminate, has been obtained. In case of laminate numbers 41/94 and 01/95 the fiber volume fraction is low as well as the laminates are observed to be resin starved. This is owing to the improper curing of the laminates i.e. though the resin content is high, it is not present in properly cured state. Also, in case of these laminates

the felt packing used during laminate preparation was of more thickness. Thus, insufficient pressure acted on the surface of the laminate.

5.3.2 Tensile strength

The ASTM standard test method for tensile properties of fiber-resin composites has the designation D 3039 (Reapproved 1982) [2]. The geometry of a specimen and end tabs with the dimensions are shown in Fig 5.3 [15].

The test has been conducted in a MTS (material testing system) machine of 10 ton capacity, at a loading rate of 0.5 mm/m in the longitudinal direction in tensile mode. The ultimate load applied on the specimen is noted from the load displacement curve and tensile strength has been determined. The initial slope of the stress-strain curve is found to obtain tensile modulus of the specimen. Table 5.2 lists the values of tensile strength, tensile modulus for various for specimens along with their fiber volume fractions.
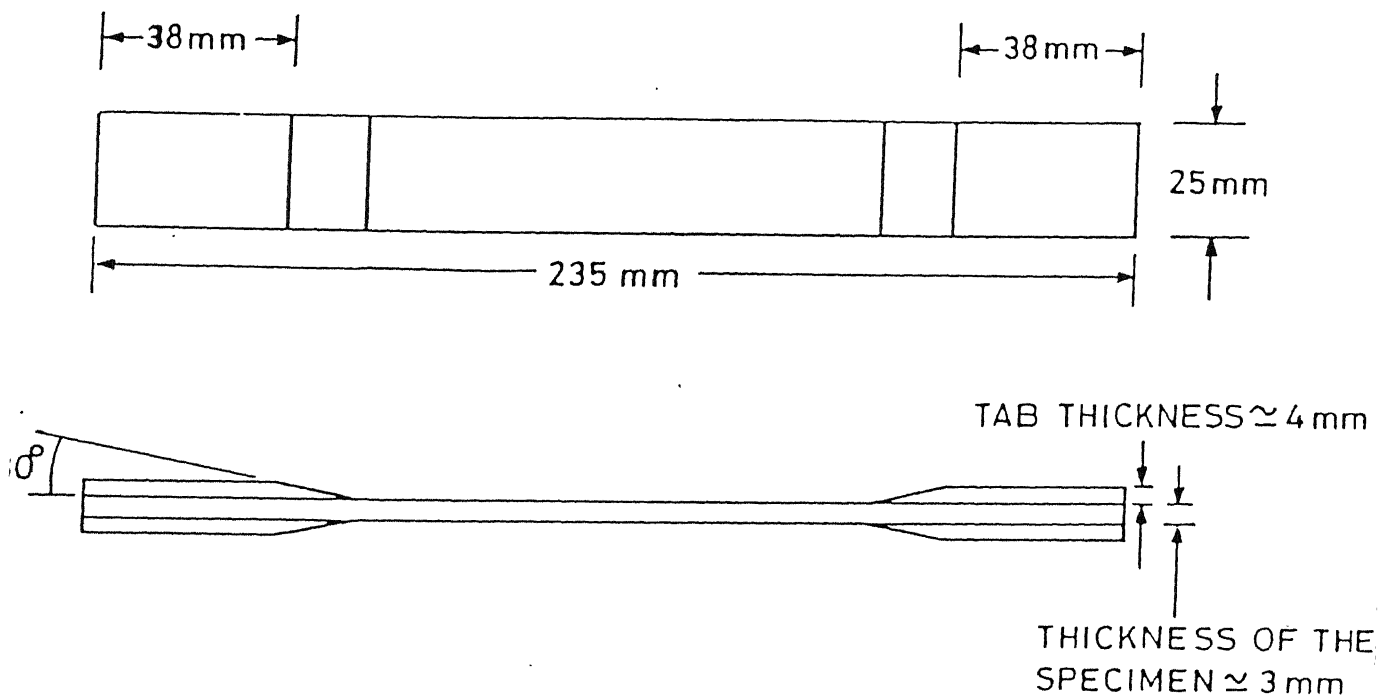
FIG. 5.3   GEOMETRY OF TENSILE STRENGTH TEST SPECIMEN.

TABLE 5.2   Tensile strength, tensile modulus of glass-fiber reinforced epoxy laminate (cross-ply)

Sl. No.	Laminate No.	V_f - %	Tensile Strength -Mpa	Tensile Modulus -GPa
1.	32/94	62.69	511.34	29.93
2.	39/94	63.50	388.51	31.71
3.	41/94 *	55.64	330.76	25.09
4.	01/95 *	52.82	341.34	25.26
5.	06/95	58.24	427.23	27.02
6.	34/94 **	60.29	806.11	44.35
7.	34/94 **	60.29	879.15	. 43.64

* Resin-starved laminate   ** Unidirectional laminate

Referring to Table 5.2, the value of tensile strength for glass fiber reinforced epoxy cross-ply laminates (Average 399.83 MPa) is 30 percent less than the corresponding value available in literature[2] which is equal to 570 MPa (Vf = 57%). The value of the tensile strength for laminate no. 32/94 is comparable. However, for rest of the laminates the values of tensile strength are on the lower side.   This could be attributed to the deteriorated quality of accelerator HT 973 owing to the completion of storage life. For laminate no. 06/95, which showed slightly better results because, the curing process has been carried out for more duration. The failure mode consistently observed has been interface matrix shear failure [2].   For unidirectional glass-fiber reinforced epoxy laminate (laminate numbers 34/94), the value of tensile strength (Average = 842.6 MPa) (V_f= 60.29%) is 24 percent less than the corresponding value given in literature [1] which is equal to 1112 MPa.

5.3.3 Compressive strength

Static uniaxial compression tests are similar to the tension test but present many more problems [2]. The biggest problem is the necessity to prevent the geometric buckling of the specimens, which can be avoided by providing multiple side supports. Compression test on unidirectional composites pose another problem when subjected to compressive loads in the fiber direction. It is the premature failure of the specimen owing to localized "brooming" at the ends.

Various loading fixtures and specimen configurations have been developed to measure the compressive strength of the composites [2]. Alignment of the test fixture and specimen are an essential considerations in any compression test.

The IITRI test fixture, as shown in the Fig. 5.4 and Fig 5.5, has been fabricated at central workshop, IIT Kanpur. It consists of upper and lower bolster. On each bolster there is a rectangular hole with two bevelled strips. Three sides of a strip are straight but other side has an angle of 78° as shown in Fig 5.4. A specimen is held between two wedge blocks. The taper of wedge blocks matches with the bevelled surfaces of the two strips, which are inserted into a rectangular hole to make it a bevelled hole. As load is applied on bolster, a high compressive stress develops between the wedge of the blocks and the specimen, thus gripping the specimen. The lower bolster has two parallel alignment pins which fit into two cylindrical holes in the upper bolster with proper allowance to ensure lateral alignment of the upper and lower bolsters. It is often realised that the system does not get started (wedge blocks slip out as soon as load is applied). To avoid this problem, the wedge blocks are bolted together with the specimen end in between, by drilling a prior hole in the either tabs of the specimen and countersunk holes in the wedge blocks, as shown in Fig. 5.4.

The geometry of the test specimen [13] is shown in Fig. 5.6. The

BEVELLED STRIP

TOP BOLSTER —

SQUARE HOLE —

WEDGE BLOCK —

BOTTOM
BOLSTER —

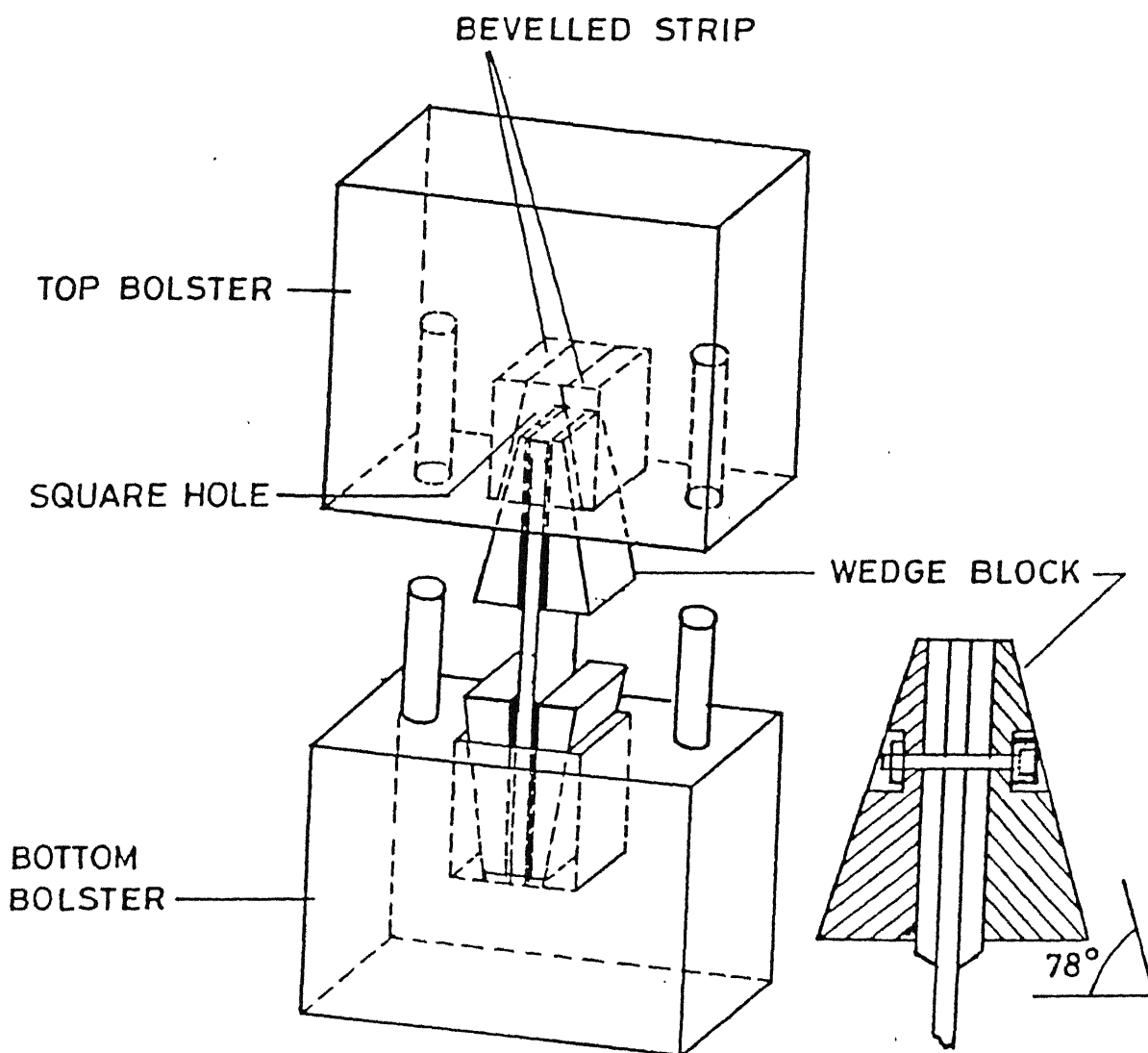78°

FIG. 5.4   COMPRESSIVE STRENGTH IITRI TEST FIXTURE.
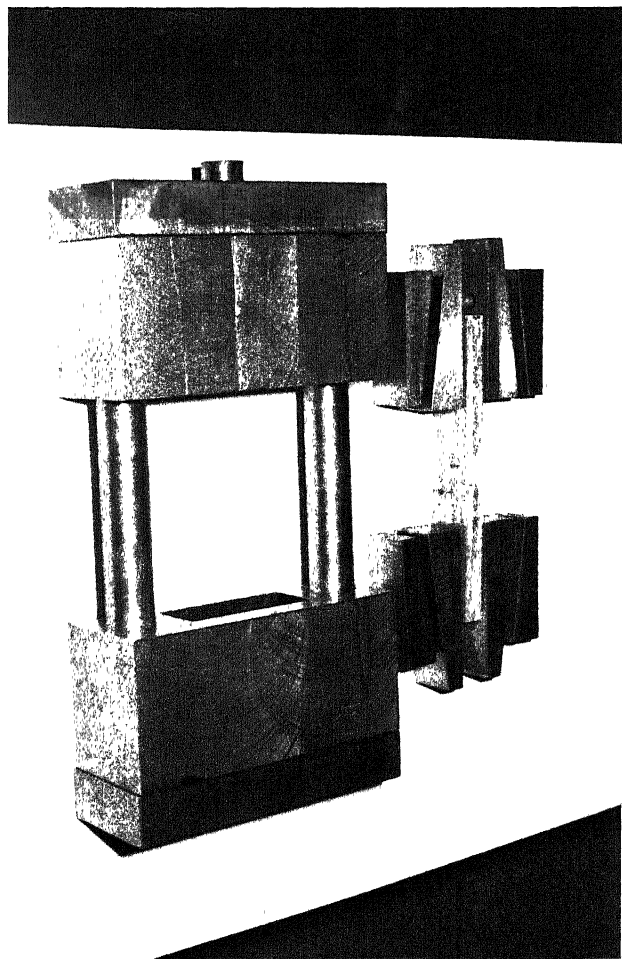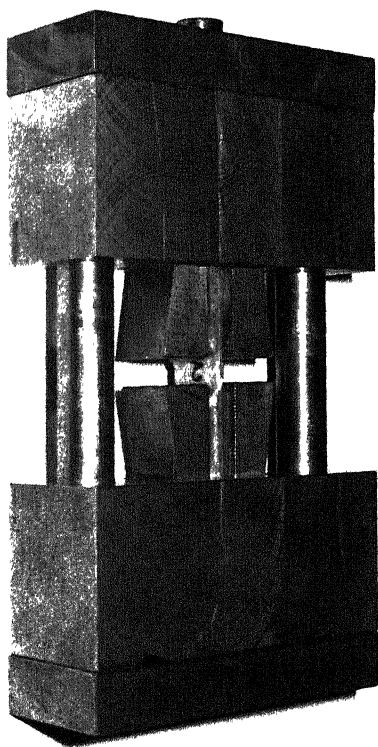
FIG. 5.5   PHOTOGRAPH SHOWING COMPRESSIVE STRENGTH
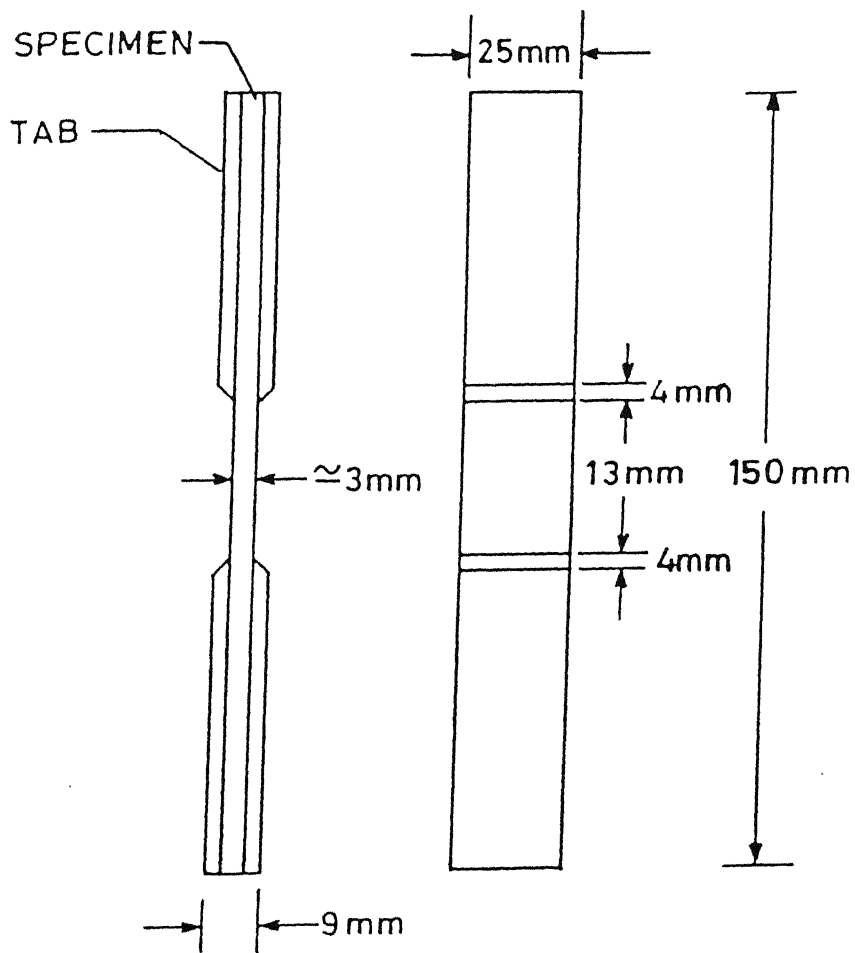   TEST FIXTURE.

FIG. 5.6   GEOMETRY OF COMPRESSIVE STRENGTH TEST SPECIMEN.

unsupported gauge length of the specimen in the IITRI compression test is deliberately made small (approximately 12 mm), so that the specimen does not buckle.

The experiment has been conducted by fitting the specimens into the fixture and then loaded in INSTRON machine of 10 ton capacity, at a rate of 0.5 mm/min. The ultimate load taken by a specimen is read from the load displacement curve. The values of compressive strength are determined for various test specimens and listed in Table 5.3.

<p align="center">Table 5.3   Compressive strength of glass-fiber reinforced
epoxy laminate</p>

Sl. No.	Laminate No.	V (%)	Compressive Strength-MPa
1.	32/94	62.69	412.4
2.	39/94	63.50	440.0
3.	41/94*	55.64	194.6
4.	01/95*	52.82	170.2
5.	06/95	58.24	542.9
6.	34/94**	60.29	766.7

*Resin-starved laminate **Unidirectional laminate

Referring to Table 5.3, for glass fiber reinforced epoxy cross-ply laminates, the average value of compressive strength, by considering laminate numbers 32/94, 39/94, 06/95 only, is 465.12 MPa, which is 10 percent less than the value given in literature [1] i.e. 521 MPa. However, the compressive strength of resin-starved laminates is very less owing to their inferior quality..

5.3.4 Interlaminar fracture toughness

Because, the composite materials are not isotropic, a sharp discontinuity in the modulii between two adjacent plies exists, leading to their delamination failure. Also, there is no through the thickness reinforcement by fibers and matrix rich zone exists at the interface. Thus, the toughness at the interface against interlaminar crack growth is very poor. Aerospace structures, a major application of composites, are found to be prone to impact loading, by which delamination failure is to be encountered. Owing to this, interlaminar fracture toughness is an important property in the field of composites. Interlaminar fracture toughness in mode I loading is characterized by critical energy release rate G_{Ic}. In this section, it has been determined experimentally by compliance method using a double cantilever beam (DCB) specimen [14].

For a cantilever beam of length a, under load P at the free end of the cantilever, total displacement u is given by:

$$u = 2\,Pa^3 / 3\,EI \qquad\qquad (5.1)$$

Where E is the Young's modulus and I is the moment of inertia of cross-sectional area of the cantilever
Compliance can be evaluated as,

$$C = u/P = 2a^3 / 3\,EI \qquad\qquad (5.2)$$

It can be shown that [14] energy release rate is given by,

$$G_I = P^2 a^2 / EI\,W$$

where W = width and a = the crack length of the specimen. For critical fracture toughness in mode I loading, the load equals to the critical load, Pc. Thus,

$$G_{Ic} = Pc^2 a^2 / EI\,W \qquad\qquad (5.3)$$

The geometry of test specimen is shown in Fig 5.7 and details about precrack introduction are given by Narayanan [14] . In the experimental, determination of critical energy release rate in mode I, G_{Ic}, the cantilever ends of a DCB specimen are pulled apart in a universal testing machine (Type-Instron capacity - 10 ton) with top cantilever attached to the fixed jaw of the machine. The lower cantilever is pulled down in the displacement control mode at a very slow speed of 0.2 mm/mm. To prevent the rotation of cantilever ends during pulling apart, a hinge [13] is provided on each side of the cantilever so as to release moment. To locate the crack tip during the experiment, both side-edges of the specimen are painted with white ink and a thin strip of graph paper is bonded on the bottom face of the specimen to observe the crack length with the help of magnifying glass. The specimen is loaded in mode I and the crack is allowed to grow by about 4-5 mm. The machine is then stopped and unloaded till the load becomes zero. The machine is reloaded to obtain the larger crack length. The cycle of loading and unloading is repeated 5-6 times and load displacement curve is obtained as illustrated in Fig. 5.8.

The data analysis [13] is carried out as follows:
Equation 5.2 can be written as

$$C = A_1 \, a^3 \tag{5.4}$$

where,

$$A_1 = 2 \, / \, 3 \, EI \tag{5.5}$$

and is constant for an experiment. Taking logarithm of eq. 5.4,

$$\ln C = \ln A_1 + 3 \ln a \tag{5.6}$$

Also, from Eq. 5.3,

$$P_c = \sqrt{GIC \; EIW} \; a^{-1} \tag{5.7}$$

$$L = 230 \text{ mm}$$
$$W = 30 \text{ mm}$$
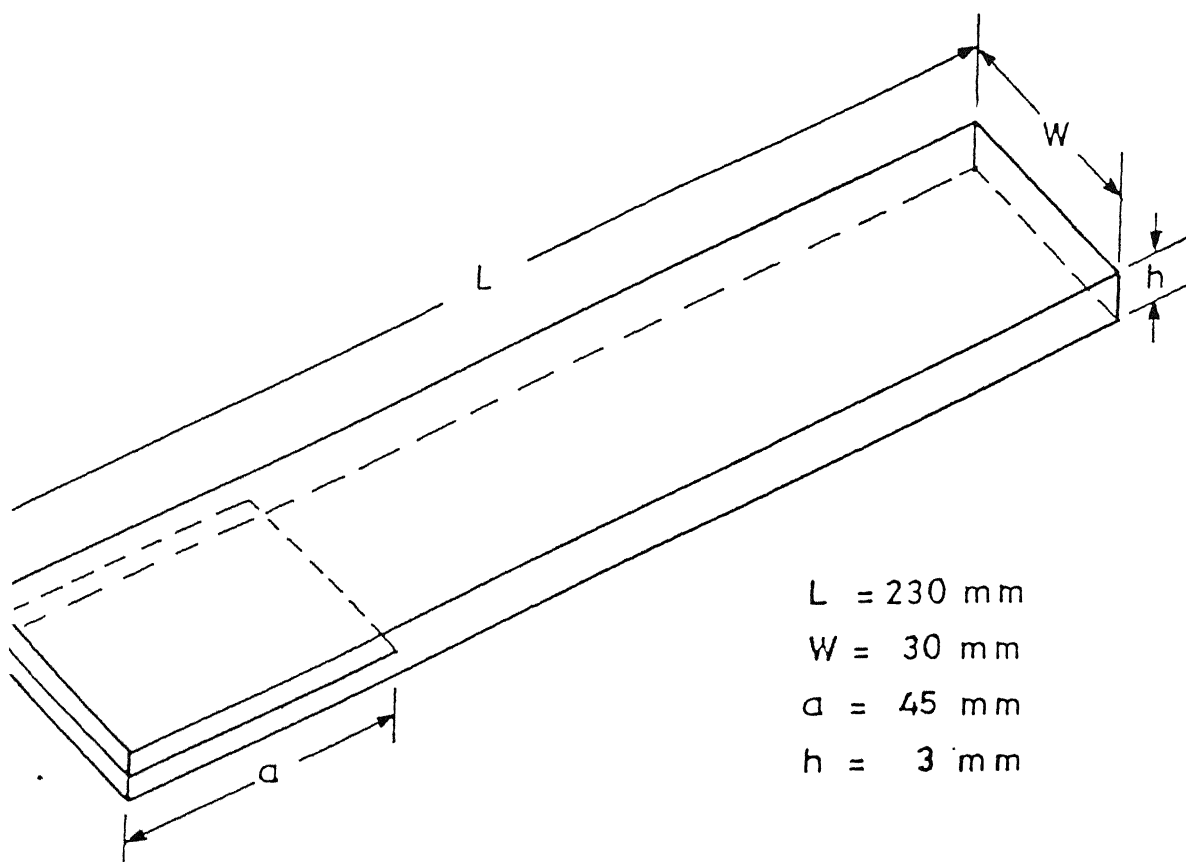$$a = 45 \text{ mm}$$
$$h = 3 \text{ mm}$$

FIG. 5.7   GEOMETRY OF TEST SPECIMEN TO DETERMINE INTERLAMINAR G_{Ic}.
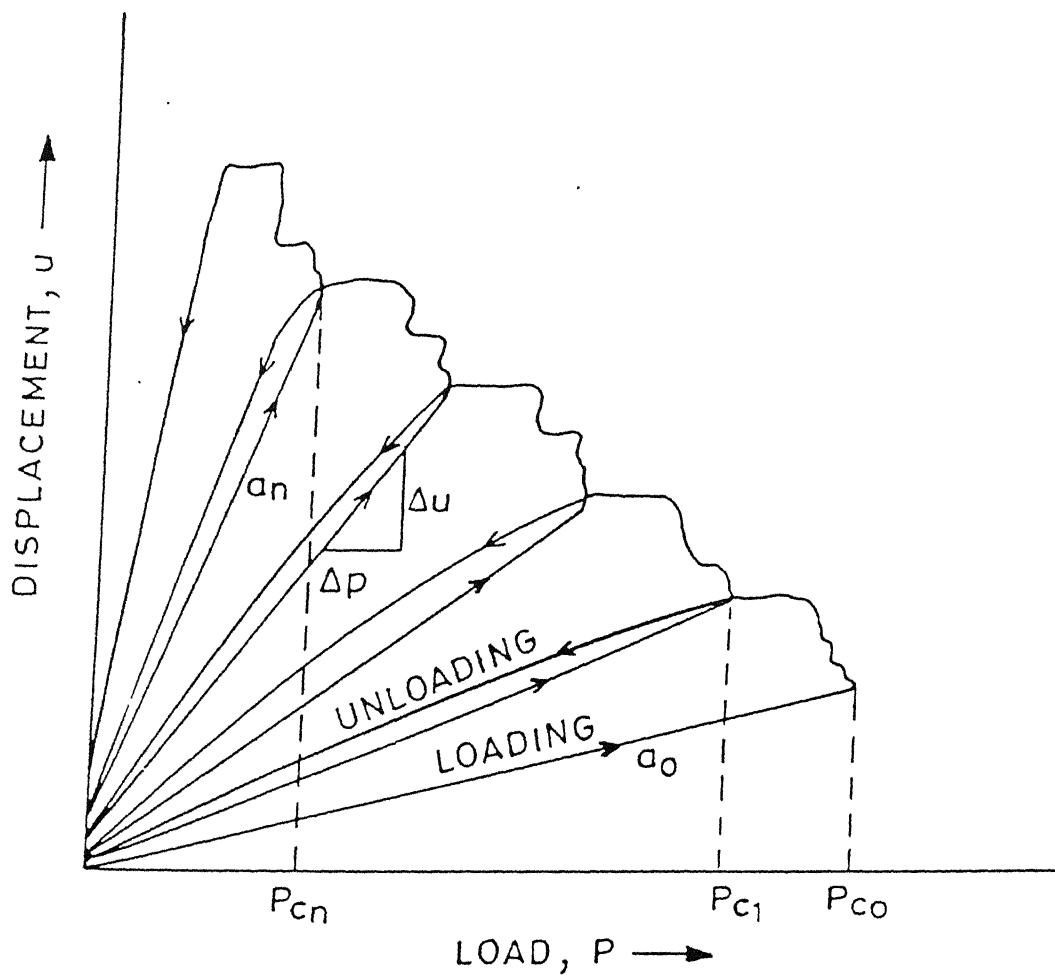
FIG. 5.8   TYPICAL LOAD-DISPLACEMENT CURVE OBTAINED IN
             INTERLAMINAR G_{Ic} DETERMINATION.

Which can be written as,

$$P_c = A_2 \, a^{-1} \tag{5.8}$$

Where $A_2 = \sqrt{GIC \ EIW}$ $\qquad$ (5.9)

which is a constant for a given specimen. Taking logarithm Eq 5.7,

$$\ln P_c = \ln A_2 - \ln a \tag{5.10}$$

eliminating EI from equations (5.5) and 5.7, we obtain,

$$G_{Ic} = 3 \, A_1 \, A_2{}^2 / \, 2 \, W \tag{5.11}$$

Thus, knowing the values of A_1 and A_2 the value of G_{Ic} for a DCB specimen can be calculated. The values of A_1 and A_2 can be found graphically. From Eq. 5.6, it is clear that ln (C) vs ln(a) plot should give a straight line of slope 3. Therefore a straight line of slope 3 is fitted to the experimental data yielding ln (A_1) as ordinate.Similarly, A_2 is found out by plotting ln (Pc) Vs ln(a) and fitting a straight line of slope -1.

Compliance C for various crack-lengths are taken from the slope of the loading part of the load displacement curves as shown in Fig. 5.7. Relations between ln (c) and ln (a), ln (Pc) and ln (a) are presented in Fig. 5.9(a) and 5.9(b) for laminate No. 22/94. Interlaminar G_{Ic} values of all the specimens with their volume fractions are listed in Table 5.4.
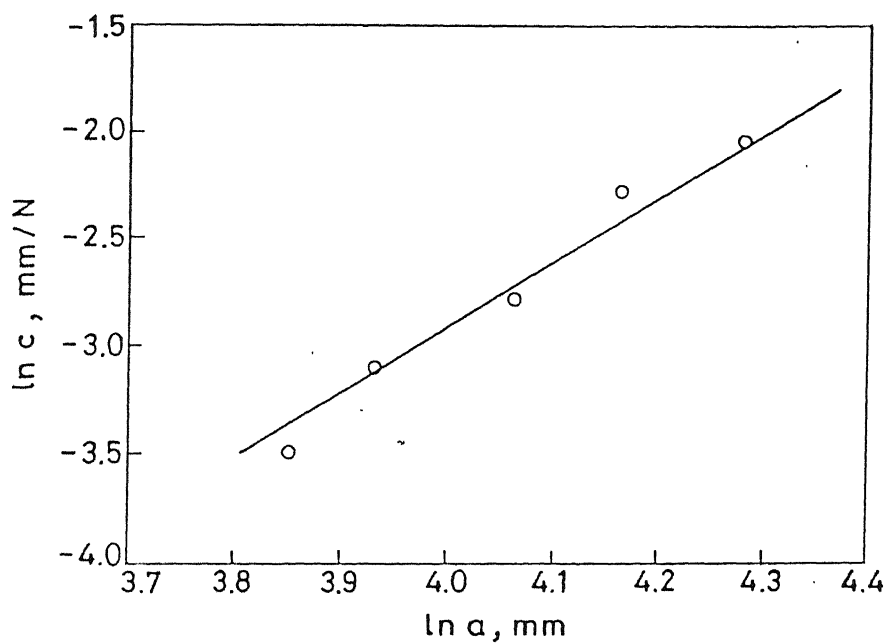
FIG. 5.9(a)   RELATION BETWEEN ln C AND ln a FOR LAMINATE
               NO. 22/94.
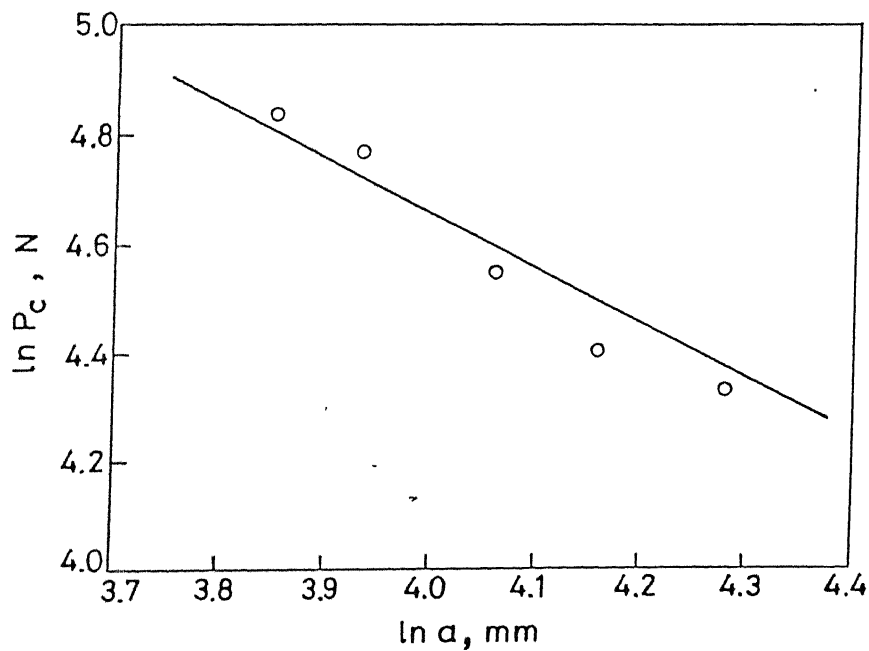

FIG. 5.9(b)   RELATION BETWEEN ln Pc AND ln a FOR LAMINATE
               NO. 22/94.

Table 5.4 Interlaminar G_{Ic} of Glass fiber reinforced epoxy laminates (cross-ply).

Sl. No.	Specimen No.	V_f (%)	Interlaminar G_{Ic} (J/m^2)
1.	22/94 *	74.65	365
2.	23/94 **	67.43	305
3.	22/94 *	74.65	532
4.	23/94 **	67.43	300
5.	06/95	58.24	324
6.	06/95	58.24	384

* without CTBN   ** With CTBN

Interlaminar G_{Ic} values of glass reinforced epoxy laminates (cross-ply) of all the specimens are given in Table 5.4 with an average of 368 J/m^2. When the values of serial no.1 and 2 are compared, it is evident that, the matrix modification with CTBN polymer as described in chapter 4, has not shown any increase in the interlaminar fracture toughness in mode I.

5.3.5 Through the thickness fracture toughness

The analysis of the failure due to existence of precrack (e.g. holes, notches) in a elasto-plastic material J-integral approach, along with other approaches, has been developed in fracture mechanics. A commonly used technique to determine J in metals is through a 3-point bend specimen, in which it can be shown that [13],

$$J = 2A \ / \ Bb$$

(5.12)

where A is the area under load displacement curve

B is the width of specimen

b is the uncracked ligament.

In this work, a modified technique with 4-point bending has been adopted. The 3-point bending formula for J can be used for 4-point bending loading condition also, which is shown by Das [13].

The experiment to determine J - integral has been conducted on a MTS machine of 10 ton capacity. The specimen geometry is given in Fig. 5.10(a) while the loading configuration of a specimen in the machine is shown in the Fig 5.10(b). The uncracked ligaments of the specimens have been measured with the help of a travelling microscope with the least count of 0.01 mm. The lengths between the two supports and two point loads of the 4-point bend test, as shown in Fig 5.11, are measured and kept constant for all the specimens. The loading of the specimen is carried out by the upper fixture at a displacement rate of 0.2 mm/min. Table 5.5. gives the values of through the thickness J_{Ic} of glass fiber reinforced epoxy laminate (cross-ply).
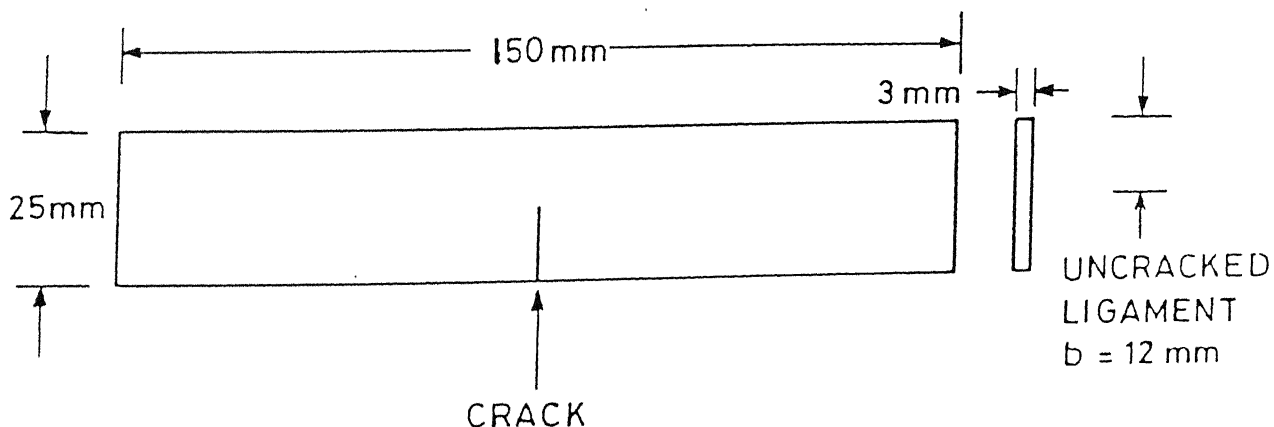
IG. 5.10(a)   GEOMETRY OF TEST SPECIMEN FOR DETERMINATION OF

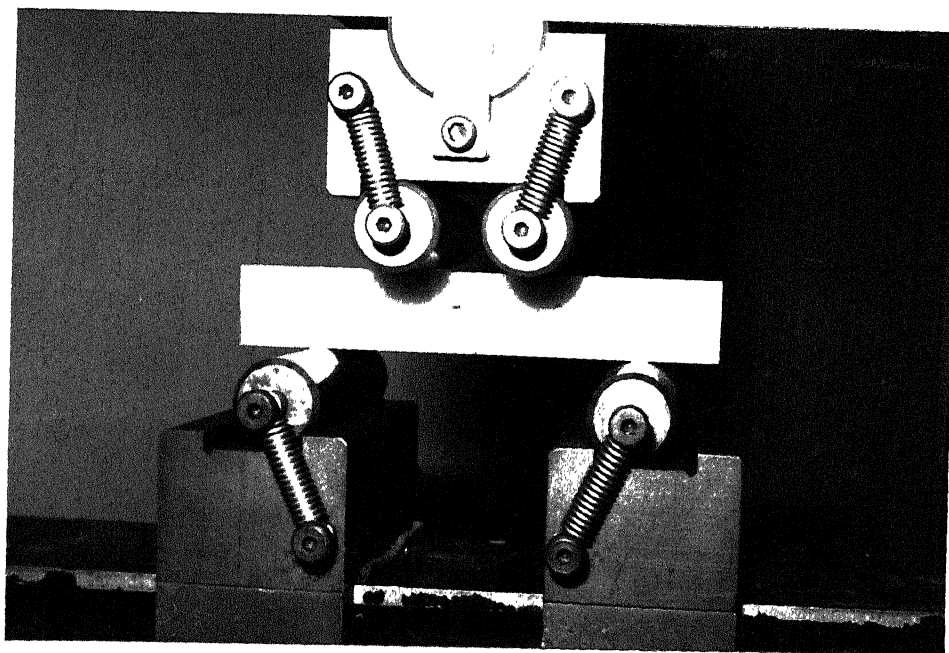FIG. 5.10(b)   LOADING CONFIGURATION IN 4-POINT BEND TEST.
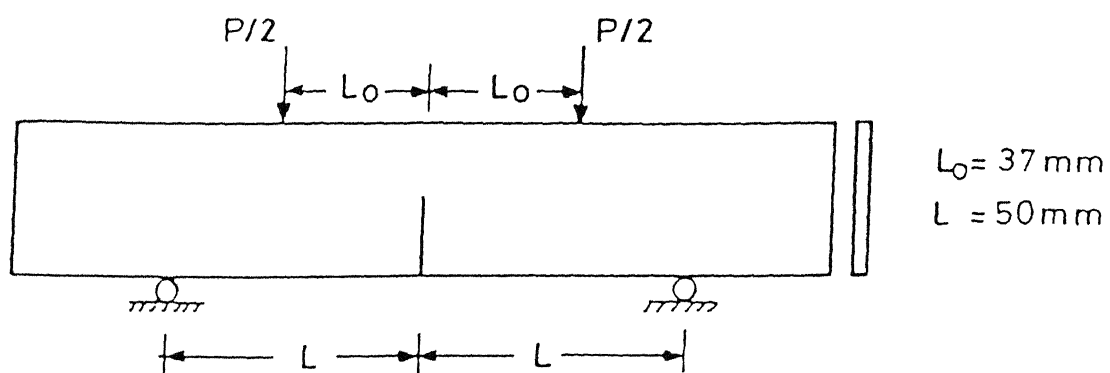

$L_0 = 37\,mm$

$L = 50\,mm$

FIG. 5.11   LENGTHS BETWEEN THE TWO SUPPORTS AND
              TWO POINT LOADS IN 4-POINT BEND TEST.

Table 5.5 Through the thickness JIC for glass fiber reinforced epoxy laminates (cross-ply)

Sl. No.	Lamin- -ate No	V_f (%)	b mm	w mm	B mm	J_{IC} KJ/m^2
1.	32/94	62.69	11.92	25.1	2.8	18.9
2.	39/94	63.50	11.96	25.0	3.6	18.3
3.	41/94*	55.64	11.89	25.00	3.4	33.4
4.	01/95*	52.82	11.78	24.90	4.0	25.5
5.	06/95	58.24	12.11	25.10	2.9	29.9

* Resin-starved laminate

Through the thickness J_{IC} for all the specimens of glass reinforced epoxy laminates (cross-ply) are given in table 5.5 with an average of 25.2 kJ/m^2 which is more than the value obtained with glass-fabric composite laminate i.e. 18.2 kJ/m^2 [13].

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

6.1 CONCLUSIONS

This work was undertaken as a part of development programme of polymer composites technology. The modifications in prepreg making machine have been carried out so as to improve the quality of prepreg tape. The performance was evaluated at every stage during modifying the assemblies. The formulation of epoxy resin mixture to develop required blends has been attempted alongwith preliminary work to enhance the fracture toughness of the resultant laminate. Laminate preparation posed various difficulties such as the understanding of curing mechanism. However, good quality laminates with fiber volume fraction close to 60%, could be prepared towards the fag end of the work. Laminate characterization determined the basic physical and mechanical properties. The value of the tensile strength for cross-ply laminate obtained during characterization is 30 percent less than the corresponding value available in literature while for unidirectional laminates, the difference is 24 percent. The value of compressive strength for cross-ply laminates is 10 percent less than corresponding value available in literature.

6.2 SUGGESTIONS FOR FUTURE WORK

Prepreg making machine needs to be modified for obtaining prepreg in proper B-stage. This could be achieved by providing a long heating chamber (tunnel oven), inside which the prepreg tape remains for 5-10 minutes at 120-130°C. Also, it is necessary to determine the extent of curing of prepreg tape in the machine.

Various auxiliary subassemblies such as system for replenishing

resin mixture to resin bath, slitter to cut the sides of the prepreg tape on the line, should be incorporated in the machine.

Tests should be conducted so as to enhance the fracture toughness of resultant laminate by modifying epoxy resin mixture.

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